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# OPTIMIZATION AND EVALUATION OF A MICROELECTROLYTIC CONDUCTIVITY DETECTOR FOR THE GAS CHROMATOGRAPHIC DETERMINATION OF PESTICIDE RESIDUES

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A microelectrolytic conductivity detector has been optimized and evaluated for the determination of halogen, nitrogen, and sulfur-containing pesticide residues in water, soil and biological samples. The influence of detector operating parameters on detector sensitivity and specificity to model compounds was investigated. Specific parameters studied included furnace temperature, reaction gas, reaction gas flow-rate, conductivity solvent, conductivity solvent flow-rate, reactor contact material, and abstracting agents. Detection limits of representative pesticides were determined for a variety of sample types using optimized detector operating conditions.

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OFFICE OF RESEARCH AND DEVELOPMENT
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# SCOPE OF WORK

## General

A microelectrolytic conductivity detector for gas chromatography was recently developed at Purdue University, West Lafayette, Indiana.[1] This detector is manufactured and marketed by Tracor, Inc., Austin, Texas; and replaces their Coulson electrolytic conductivity detector. The detector is selective to halogen-, sulfur- and nitrogen-containing compounds, and has subnanogram sensitivity with a relatively wide linear dynamic range.

The high sensitivity, selectivity and linearity of the detector should make it a valuable analytical instrument for contaminant monitoring. However, since the detector has been available for only a short time, the analytical potential of this device is not known. It was the purpose of this contract to optimize and fully evaluate the microelectrolytic conductivity detector for the sensitive detection of nitrogen-, halogen- and sulfur-containing pesticides in environmental samples.

## Specifics

In performance of the technical effort, the Contractor has:

a. Optimized and evaluated the detector for the determination of chlorinated hydrocarbons (pesticides and toxic substances) in water, soil and animal tissue substrates at the most sensitive practical levels of detection.

b. Demonstrated the usefulness of the detector for differentiating between chlorinated hydrocarbon pesticides and polychlorinated biphenyls and polychlorinated naphthalenes at the residue level using environmental and biological samples.

c. Optimized and evaluated the detector system for selective, subnanogram sensitivity to nitrogen-containing compounds in a representative variety of sample types, including water, soil and biological tissues.

d. Optimized and evaluated the detector for selective, subnanogram sensitivity to sulfur-containing pesticides in a representative variety of sample types, including water, soil and biological tissues.

e. Demonstrated the linearity of response, reliability and ease of operation.

f. Delivered two modified detector systems to the Project Officer.

## DETECTOR OPERATION

### Experimental Conditions

Apparatus. Tracor Model 310 Hall electrolytic conductivity detectors and laboratory prototype detectors were used throughout this study. The commercial detector was modified by incorporating a solvent vent and decreasing the recorder attenuator factor of the conductivity meter from a value of 1.0 to 0.1. The solvent vent was constructed from a 1/8-inch stainless steel union by the addition of a 0.0625 inch o.d. X 0.03 inch i.d. X 2 ft. vent tube. The end of the vent tube was connected to a Whitney toggle valve (0.080 inch orifice). A Teflon restrictor tube (1/16 inch o.d. X 0.02 inch i.d.) was connected to the valve exit to provide sufficient back pressure so that the carrier gas was vented and the reaction gas was not. The solvent vent was interfaced to the chromatograph via 1/8-inch o.d. glass-lined stainless steel tubing. The recorder attenuator factor was decreased by reducing the value of the voltage divider resistor prior to the attenuator circuit from 1.24 M to 124 K.

Chromatography. Halogen- and sulfur-containing pesticides were analyzed using 1/4-in. o.d. X 2-mm. i.d. X 6-ft. glass columns containing 5% OV-101 on 80-100 mesh Gas Chrom Q operated at 210° and a helium carrier gas flow of 30-40 cc/min. Nitrogen containing pesticides were analyzed using 1/4-in. o.d. X 2-mm. i.d. X 6-ft. silanized glass columns containing 1% Carbowax 20M operated at 160 or 190° with a hydrogen carrier gas flow rate of 40 cc/min.

Tracor Models MT-220 and 550 gas chromatographs were used for the analysis of halogen and sulfur pesticides. A Varian Model 1200 gas chromatograph was used for the analysis of nitrogen pesticides. The inlet, outlet and transfer temperatures on the MT-220 were 225, 235 and 245° respectively. The inlet and outlet temperatures on the 550 were 235 and 275°. The Varian chromatograph inlet and outlet temperatures were 200$^{o}$. The hydrogen gas used in the catalytic reductive modes (halogen and nitrogen) was generated with an Elhygen hydrogen generator.

## Detection of Halogen Containing Compounds

Optimization of Detector Operating Conditions. Halogen-containing compounds are detected as the strong acid HX. Chlorine containing compounds can be converted to HCl by pyrolysis (with only inert carrier gas), reductive pyrolysis, oxidative pyrolysis, catalytic reduction or catalytic oxidation. Quartz tubing is used in the pyrolytic modes, whereas nickel tubing is used in the catalytic modes. Hydrogen is used as the reaction gas for the reductive modes and either air or oxygen for the oxidative modes.

"Conductivity Solvent and Reaction Systems". The detection of trace quantities of chlorine-containing compounds presents a number of problems. First, the chlorinated compound must be converted to HCl at a temperature of 600-950$^{o}$. At this temperature, most materials have considerable surface reactivity, and great care must be exercised to prevent HCl absorption. Second, HCl is very reactive and must be transported to the conductivity cell via an "inert" path. Third, HCl is a strong acid and impurities in the conductivity solvent may be protonated, which can result in peak tailing and a loss in sensitivity.

Ideally, the conductivity solvent should be compatible with the ion exchange resin, have a very low conductivity, effectively support conductance of the monitored species, and present no health hazard. In an attempt to find an appropriate solvent for the detection of halogen-containing compounds, a wide variety of protic and aprotic solvents were investigated.

Solvents were evaluated for specificity, linearity and sensitivity of response using a "selectivity" sample mixture and a "pesticide" sample mixture. The selectivity mixture was comprised of 2 μg of hexadecane, 100 ng of caffeine, 100 ng of parathion, 2 ng of heptachlor epoxide and 100 ng of ethyl stearate. The pesticide mixture included lindane, heptachlor, aldrin, heptachlor epoxide and dieldrin. The pesticide quantities ranged from $1 \times 10^{-10}$ g to $1 \times 10^{-6}$ g of each component.

Hexadecane was used to evaluate detector selectivity against hydrocarbons. Caffeine, parathion and ethyl stearate represented compounds containing nitrogen, sulfur and ester groups respectively. The compounds are unique in the respect that they represent classes of compounds which exhibit a response considerably greater than that of most other classes of compounds containing these elements. Thus, they represent the greatest degree of interference that should be encountered in the determination of halogen-containing compounds.

Detector sensitivity and selectivity were determined for the conductivity solvents methyl alcohol, 50% ethyl alcohol, ethyl alcohol, isopropyl alcohol, acetonitrile, diisopropyl ketone, nitroethane, nitrobenzene, benzene and dimethyl formamide. Detector linearity to chlorinated hydrocarbon pesticides was then determined for those solvents that exhibited good sensitivity and selectivity. The evaluation was conducted in the pyrolytic mode using hydrogen as the reaction gas and a 2-mm. i.d. quartz reaction tube.

In general, absolute alcohols, and acetonitrile were the only solvents which gave both high sensitivity and linearity of response. (See Figure 1-3). Acetonitrile appeared to alter the ion exchange resin and gave erratic results. Dimethyl formamide and diisopropyl ketone were not

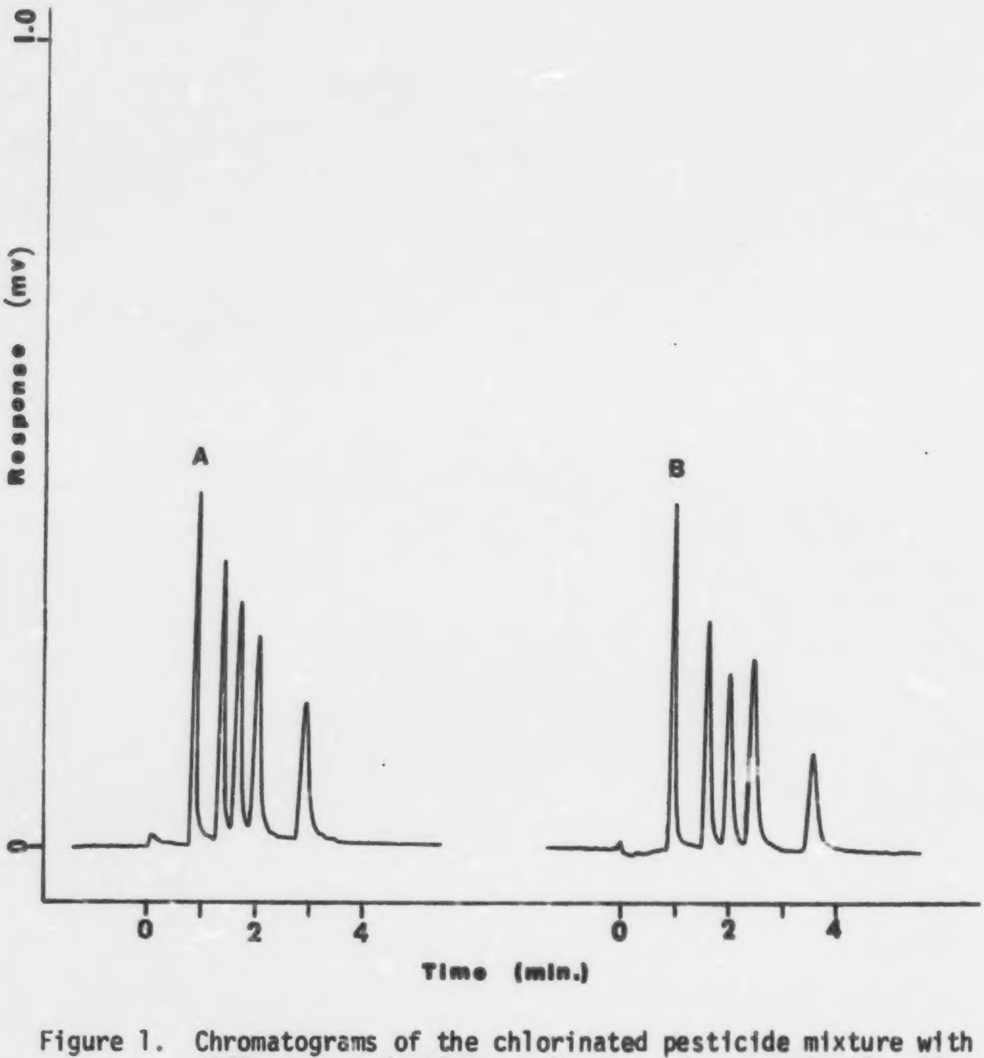

Figure 1. Chromatograms of the chlorinated pesticide mixture with different conductivity solvents: A, acetonitrile, 20 ng of each compound, 100 X 0.8; B, methyl alcohol, 10 ng of each compound, 10 X 3.2.

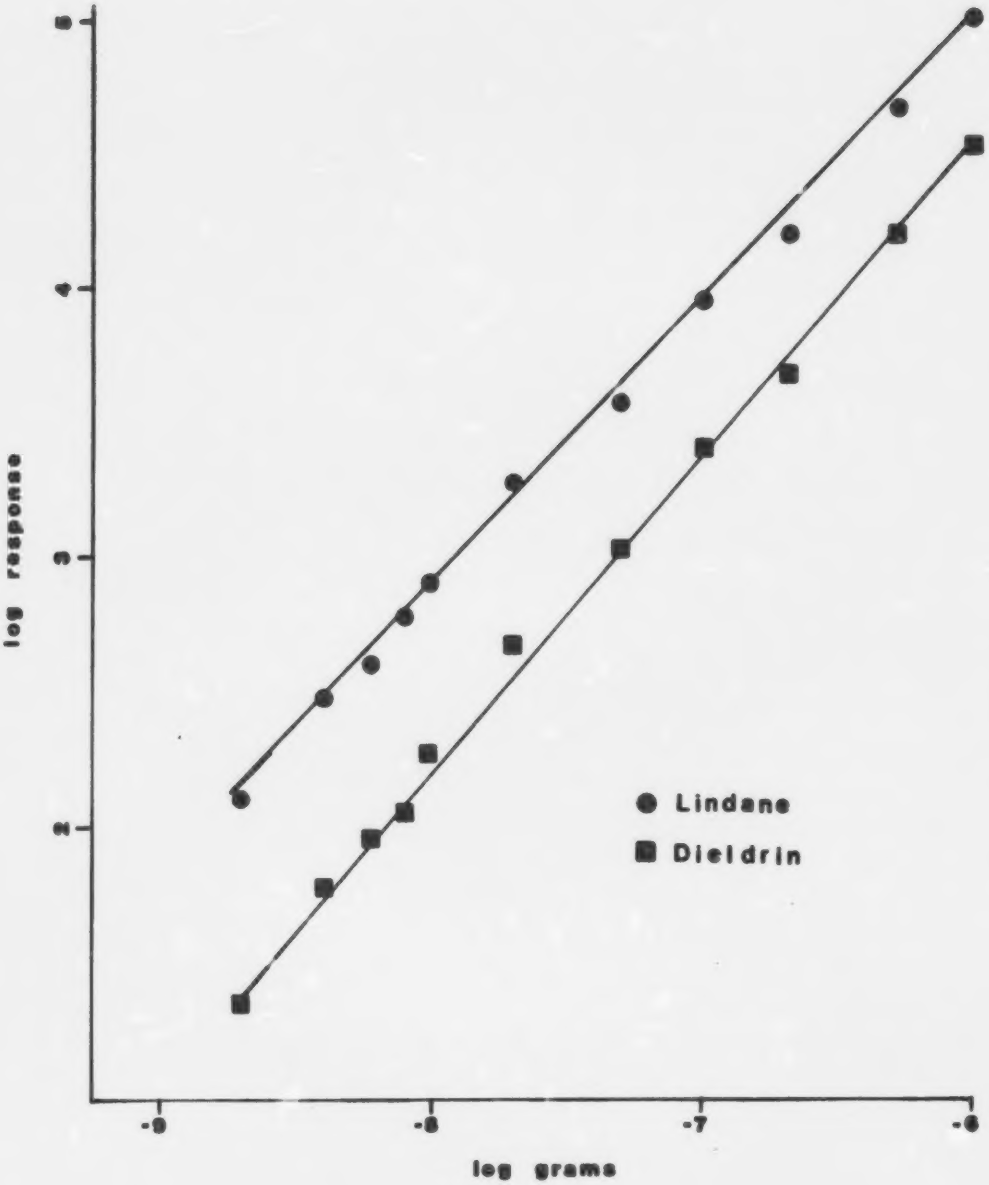

Figure 2. Linearity of response to lindane and dieldrin. Conditions: furnace temperature, 700$^{o}$; $H_2$ reaction gas, 0 cc/min; conductivity solvent, methyl alcohol; resin, IRN-150/77.

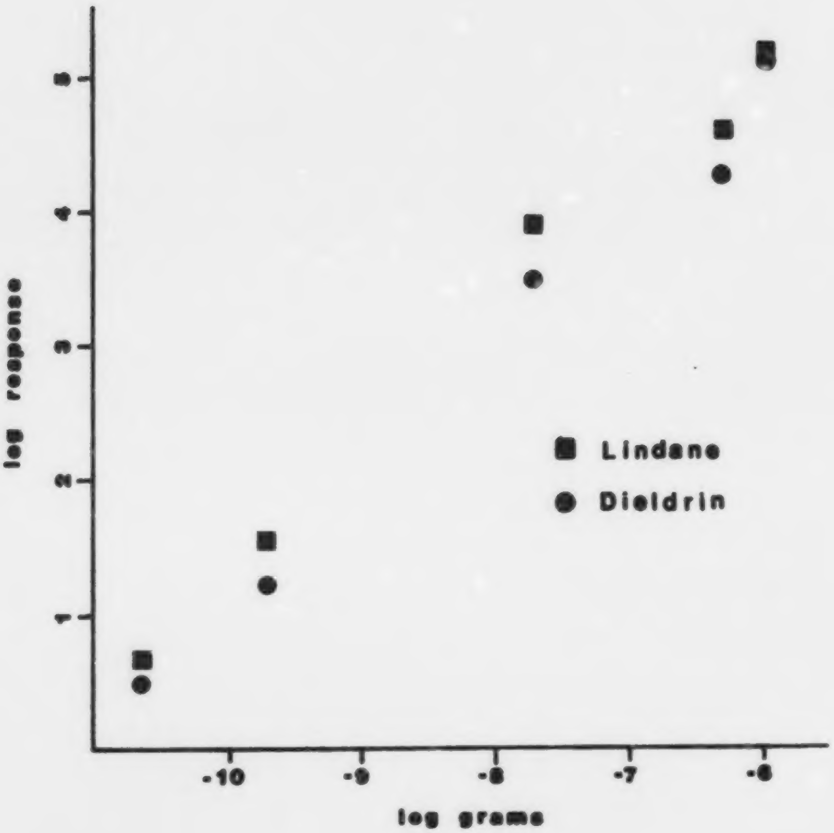

Figure 3. Linearity of response to lindane and dieldrin. Conditions: furnace temperature, $900^{\circ}$; $H_2$ reaction gas; 5 cc/min, conductivity solvent, acetonitrile; resin, ARM-381.

compatible with the ion exchange resin and gave too high of a background to be evaluated. Although selectivity for chlorine-containing compounds against hydrocarbons was good, selectivity against caffeine, parathion and ethyl stearate was poor for all the solvents investigated.

Selectivity for halogen-containing compounds (exemplified by heptachlor epoxide) as a function of the conductivity solvent is shown for selected solvents in Table I. The solvents listed in this table represent potentially useful conductivity solvents and displayed good sensitivity and linearity, with the exception of nitrobenzene which exhibited very poor linearity for quantities of heptachlor epoxide greater than approximately 25 ng. Very little or no response was observed for hexadecane for all the solvents investigated. Consequently, selectivities for heptachlor epoxide versus hexadecane are reported as being greater than the selectivity that would be calculated if the hexdecane response was twice that of the noise level. Thus, Table I does not imply that the use of ethyl alcohol as the conductivity solvent will result in greater selectivity for halogen-containing compounds relative to hydrocarbons than will any of the other solvents.

Since the conducting species created from caffeine and parathion are not known, selectivities were calculated based upon the response in peak height per gram of substance. These values therefore do not represent absolute selectivities and should not be compared with data from other studies unless specifically stated.

It can be seen from the data in Table I that hydrocarbons will give very little interference in the determination of chlorine-containing compounds. However, certain other compounds can give a significant response that is not

Table I. Relative Selectivity for Halogen-Containing Compounds versus Various Types of Compounds as a Function of the Conductivity Solvent.[a,b]

| Solvent[c] | n-$C_{16}H_{34}$ | Caffeine | Parathion | Ethyl Stearate |
|---|---|---|---|---|
| 50% EtOH | >42,000 | 26 | 18 | 54 |
| EtOH | >79,000 | 51 | 43 | 161 |
| i-PrOH | >34,500 | 62 | 111 | 173 |
| Nitrobenzene | >32,000 | 400 | 640 | >1600 |
| Acetonitrile | > 5,500 | 4 | 9 | 28 |

[a] Quartz reaction tube was 2 mm. i.d., furnance temperature was 950°, and the hydrogen reaction gas flow rate was 5 cc/min.

[b] Selectivities were calculated from peak heights per gram of substance.

[c] The ion exchange resin tube was packed with 50% Amberlite IRN-150 (cell side) and 50% Amberlite IRN-77 (pump side).

greatly influenced by most of the conductivity solvents investigated. (See Figure 4). Solvents such as nitrobenzene and nitroethane can increase the selectivity for halogen-containing compounds. These solvents, however, display very poor linearity of response and are not practical to use.

In general, absolute alcohols give the best performance for the determination of halogen compounds. They are compatible with the ion exchange resin, give good sensitivity and provide a wide linear dynamic range. Selectivity, although good against hydrocarbons, may not be sufficient for certain other types of compounds, and as shown in Table I, selectivity can be as low as 10 to 100.

In an effort to enhance selectivity, the effects of reaction gas flow rate and furnace temperature are investigated. A 1:1 ethyl alcohol/water conductivity solvent was used so that the response from any weak acids or bases (i.e. $CO_2$, $NH_3$) would not be leveled and the influence of the reaction conditions more readily seen.

Detector responses to heptachlor epoxide and a variety of non-halogen compounds as a function of furnace temperature and hydrogen reaction gas flow rate are shown in Tables II-IV. Since there are a number of variables such as condition of the reaction tube, the cleanliness of the Teflon transfer line and the occurance of ion exchange resin bleed which can influence detector response, the data in these tables should only be used for qualitative comparisons and the determination of response trends.

Response to heptachlor epoxide increases with an increase in furnace temperature and is approximately three times as large at $950^{o}$ as at $700^{o}$. Caffeine also displays a similar but more positive temperature relationship. Response to ethyl stearate increases with temperature to a maximum at $875^{o}$ and then decreases

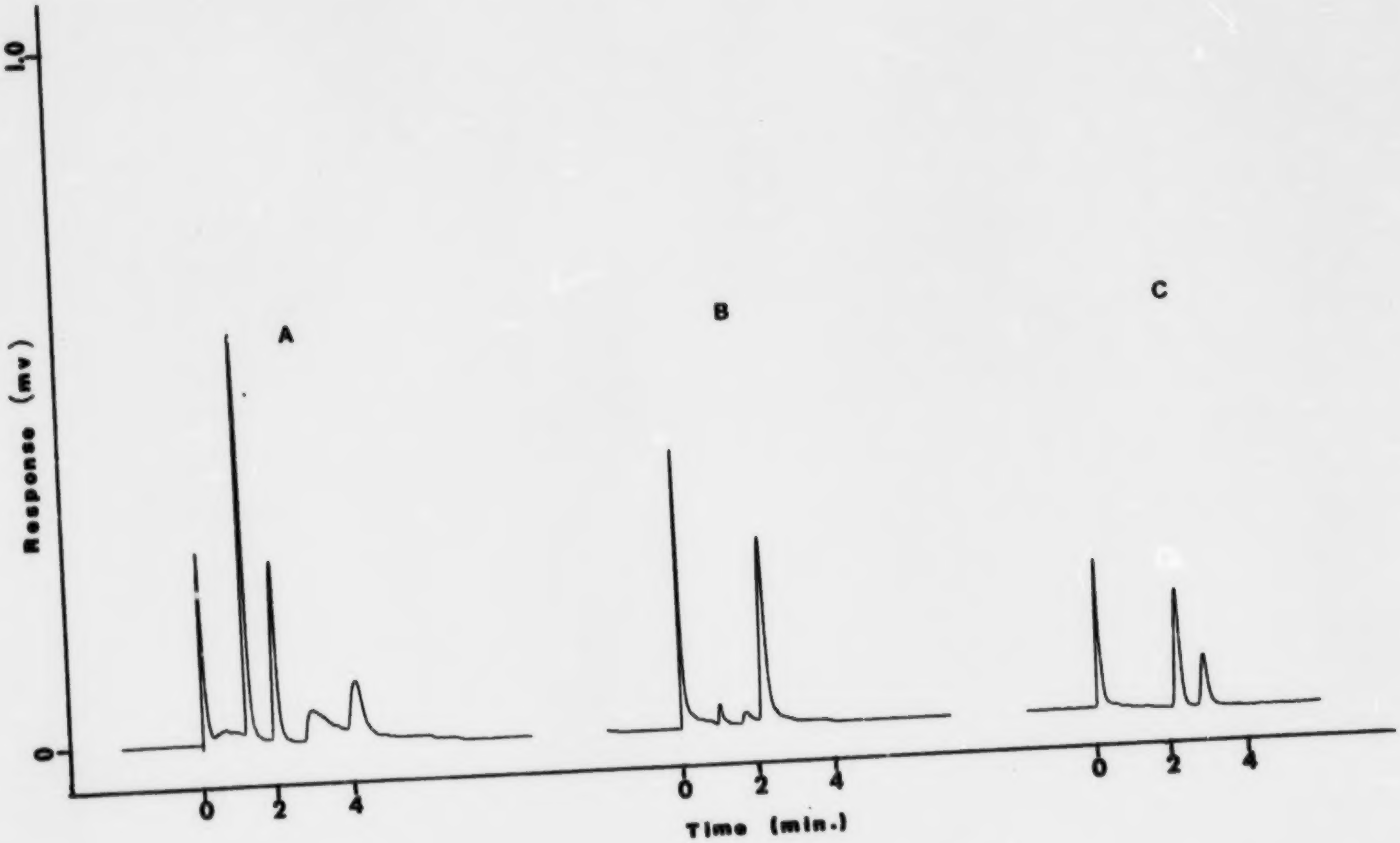

Figure 4. Chromatograms of the selectivity mixture with different conductivity solvents. Conditions: furnace temperature, 950$^0$; $H_2$ reaction gas, 5 cc/min; conductivity solvent; A = acetonitrile, B = nitrobenzene, C = methyl alcohol.

Table II. Influence of Furnace Temperature on Detector Response in the Pyrolytic Mode Using No Reaction Gas[a].

| Compound | Furnace Temperature ($^oC$) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 700 | 750 | 800 | 825 | 850 | 875 | 900 | 925 | 950 |
| Hept. Epox. | 970 | 970 | 1170 | 1170 | 1680 | 1850 | 2180 | 2110 | 2560 |
| Parathion | 50 | 70 | 96 | 92 | 132 | 132 | 139 | 114 | 114 |
| Caffeine | ND[b] | ND | 5 | 11 | 23 | 50 | 50 | 52 | 66 |
| Ethyl Stearate | ND | 6 | 25 | 54 | 90 | 97 | 97 | 72 | 57 |
| Hexadecane | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| Thioanisole | 13 | 27 | 50 | 65 | 71 | 73 | 53 | 50 | 49 |
| _N_,_N_-diethyl-_p_-anisidine | 6 | 3 | 2 | 2 | 2 | 3 | 3 | 3 | 3 |

[a] Response is in mho-sec/gram. The conductivity solvent was 1:1 $EtOH/H_2O$ at a flow rate of 0.5 cc/min.

[b] ND = No response detected.

Table III. Influence of Furnance Temperature on Detector Response in the Pyrolytic Mode Using 5 cc/min Hydrogen Reaction Gas[a].

| Compound | Furnace Temperature ($^{o}$C) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 700 | 750 | 800 | 825 | 850 | 875 | 900 | 925 | 950 |
| Hept. Epox. | 630 | 810 | 840 | 1180 | 1390 | 1520 | 1910 | 2020 | 2740 |
| Parathion | 22 | 37 | 42 | 44 | 38 | 29 | 24 | 23 | 27 |
| Caffeine | ND[b] | 2 | 7 | 10 | 24 | 27 | 36 | 38 | 46 |
| Ethyl Stearate | ND | 10 | 40 | 87 | 121 | 124 | 100 | 71 | 47 |
| Hexadecane | ND | ND | ND | ND | 0.01 | 0.01 | ND | ND | ND |

[a] Response is in mho-sec/gram. The conductivity solvent was 1:1 EtOH/$H_2O$ at a flow rate of 0.5 cc/min.

[b] ND = No response detected.

Table IV. Influence of Furnace Temperature on Detector Response in the Pyrolytic Mode Using 50 cc/min. Hydrogen Reaction Gas[a].

| Compound | Furnace Termperature ($^oC$) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 700 | 750 | 800 | 825 | 850 | 875 | 900 | 925 | 950 |
| Hept. Epox. | 710 | 1080 | 1120 | 1120 | 1120 | 960 | 1050 | 1340 | 2140 |
| Parathion | 32 | 27 | 27 | 23 | 25 | 21 | 17 | 15 | 20 |
| Caffeine | ND[b] | ND | ND | ND | 5 | 13 | 20 | 30 | 37 |
| Ethyl Stearate | ND | 2 | 39 | 74 | 133 | 142 | 121 | 98 | 76 |
| Hexadecane | ND | 0.01 | 0.01 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 |
| Thioanisole | 9 | 28 | 49 | 58 | 58 | 55 | 54 | 54 | 50 |
| *N*,*N*-diethyl-*p*-anisidine | 5 | 8 | 10 | 12 | 10 | 10 | 9 | 10 | 7 |

[a] Response is in mho-sec/gram. The conductivity solvent was 1:1 EtOH/$H_2O$ at a flow rate of 0.5 cc/min.

[b] ND = No response detected.

to approximately 50% of the maximum value. Although parathion and thioanisole represent different classes of sulfur compounds, they exhibit similar temperature trends. In the absence of hydrogen reaction gas, they reach a maximum positive response between 850 to 900$^0$, whereas in the presence of reaction gas they exhibit a slight negative temperature relationship from 800 to 950$^0$.

Although the presence of hydrogen reaction gas slightly alters the temperature relationships for some of the compounds, particularly the sulfur-containing compounds, selectivity to heptachlor epoxide is not significantly increased (See Tables V-VII). In fact, selectivity is slightly decreased by the presence of hydrogen reaction gas for ethyl stearate, thioanisole and N, N-diethyl-p-anisidine. Representative chromatograms for the selectivity mixture are shown in Figure 5 and 6.

The data in Tables V-VII indicate that selectivity to halogen compounds may be greater at temperatures in excess of 950$^0$ since the selectivity values increase for all compounds from 900 to 950$^0$. Thus, a high temperature furnace was constructed so that this potential increase in selectivity could be investigated. The furnace had a heated zone of approximately 1 inch and employed a platinum-10% rhodium heating element which was encased in Transite insulation (0.75 in. thick). Furnace temperatures were determined from an applied voltage-temperature curve.

Results obtained with this furnace operated at 1100$^0$ and a hydrogen reaction gas flow rate of 5 cc/min. are summarized in Table VIII. Under these conditions, 100 ng of ethyl stearate produces no visible response, and selectivity is $> 10^3$ (calculated using a value of 2 mho-sec/gram). Selectivity versus parathion and caffeine is also improved and increases from methyl to isopropyl alcohol as the conductivity solvent (See Figure 7). Selectivity to heptachlor epoxide can be further improved by increasing the hydrogen flow rate (See Figure 8).

Table V. Influence of Furnace Temperature on Specificity of Response to Heptachlor Epoxide Relative to Various Compounds in the Pyrolytic Mode Using no Reaction Gas[a].

| Compound | Furnace Temperature | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 700 | 750 | 800 | 825 | 850 | 875 | 900 | 925 | 950 |
| Hept. Epox. | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| Parathion | 19 | 14 | 12 | 13 | 13 | 14 | 16 | 19 | 22 |
| Caffeine | >940 | >940 | 234 | 106 | 73 | 37 | 44 | 41 | 39 |
| Ethyl Stearate | >320 | 162 | 47 | 23 | 19 | 19 | 22 | 29 | 45 |
| Hexadecane | >97,000 | >97,000 | >117,000 | >117,000 | >168,000 | >185,000 | >218,000 | >211,000 | >256,000 |
| Thioanisole | 75 | 36 | 23 | 18 | 24 | 25 | 41 | 42 | 52 |
| *N*,*N*-diethyl-*p*-anisidine | 162 | 323 | 585 | 585 | 840 | 617 | 727 | 703 | 853 |

[a] The conductivity solvent was 1:1 $EtOH/H_2O$

Table VI. Influence of Furnace Temperature on Specificity of Response to Heptachlor Epoxide Relative to Various Compounds in the Pyrolytic Mode Using 5 cc/min of Hydrogen Reaction Gas[a].

| | Furnace Temperature | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Compound | 700 | 750 | 800 | 825 | 850 | 875 | 900 | 925 | 950 |
| Hept. Epox. | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| Parathion | 29 | 22 | 20 | 27 | 37 | 52 | 80 | 88 | 101 |
| Caffeine | >405 | 405 | 120 | 118 | 58 | 56 | 53 | 53 | 60 |
| Ethyl Stearate | >400 | 81 | 21 | 14 | 11 | 12 | 19 | 28 | 58 |
| Hexadecane | >63,000 | >81,000 | >84,000 | >118,000 | 139,000 | 152,000 | >191,000 | >202,000 | >274,000 |

[a] The conductivity solvent was 1:1 $EtOH/H_2O$

Table VII. Influence of Furnace Temperature on Specificity of Response to Heptachlor Epoxide Relative to Various Compounds in the Pyrolytic Mode Using 50 cc/min of Hydrogen Reaction Gas[a].

| Compounds | Furnace Temperature ($^oC$) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 700 | 750 | 800 | 825 | 850 | 875 | 900 | 925 | 950 |
| Hept. Epox. | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| Parathion | 22 | 40 | 41 | 49 | 45 | 46 | 62 | 89 | 107 |
| Caffeine | >355 | >540 | >560 | >560 | 224 | 74 | 53 | 45 | 58 |
| Ethyl Stearate | >355 | 540 | 29 | 15 | 8 | 7 | 9 | 14 | 28 |
| Hexadecane | >71,000 | 108,000 | 112,000 | 56,000 | 56,000 | 48,000 | 52,500 | 67,000 | 107,000 |
| Thioanisole | 79 | 39 | 23 | 19 | 19 | 17 | 19 | 25 | 43 |
| _N_,_N_-diethyl-_p_-anisidine | 142 | 135 | 112 | 93 | 112 | 96 | 117 | 134 | 306 |

[a] Response is in mho-sec/gram. The conductivity solvent was 1:1 $EtOH/H_2O$ at a flow rate of 0.5 cc/min.

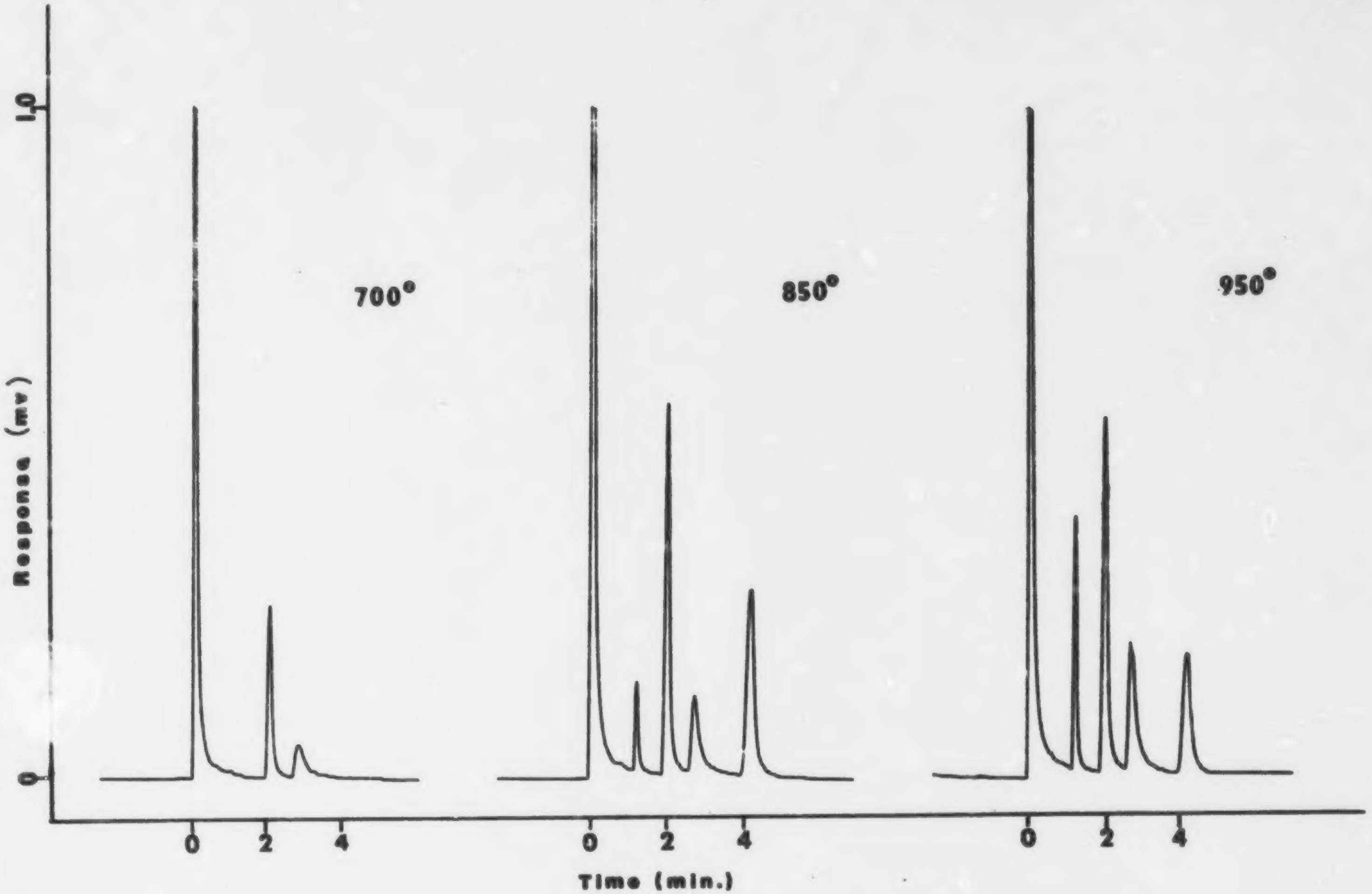

Figure 5. Chromatograms of the selectivity mixture at different furnace temperatures. Conditions: $H_2$ reaction gas, 0 cc/min; conductivity solvent, 50% ethyl alcohol; resin, ARM-381; attenuation, 3 X 0.8.

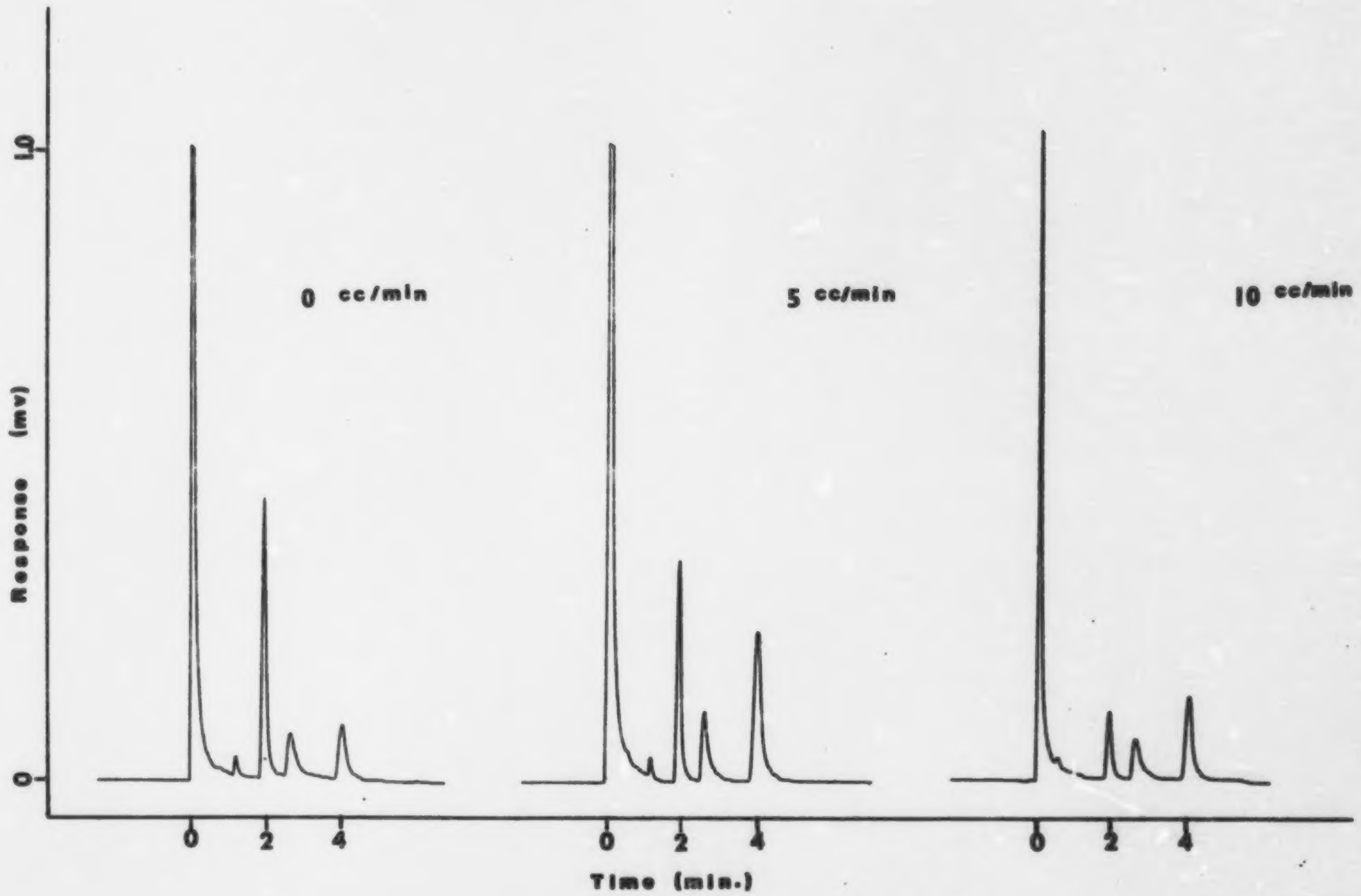

Figure 6. Chromatograms of the selectivity mixture at different $H_2$ reaction gas flow rates. Conditions: furnace temperature, 800°; conductivity solvent, 50% ethyl alcohol; attenuation, 3 X 0.4.

Table VIII. Influence of Conductivity Solvent on Specificity of Response to Heptachlor Epoxide Relative to Various Compounds in the Pyrolytic Mode Using a Furnace Temperature of 1100°C and 5 cc/min of Hydrogen Reaction Gas.

| Solvent | Selectivity[a] | | | |
|---|---|---|---|---|
| | $n\text{-}C_{16}$ | Caffeine | Parathion | Ethyl Stearate |
| Methyl Alcohol | >363,000[b] | 24 | 138 | >3,600[c] |
| Ethyl Alcohol | >360,000 | 38 | 136 | >3,400 |
| Isopropyl Alcohol | >140,000 | 71 | 265 | >1,400 |

[a] Calculated from response in mho-sec/gram.

[b] Calculated using a lower value of 0.02 mho-sec/gram.

[c] Calculated using a lower value of 2 mho-sec/gram.

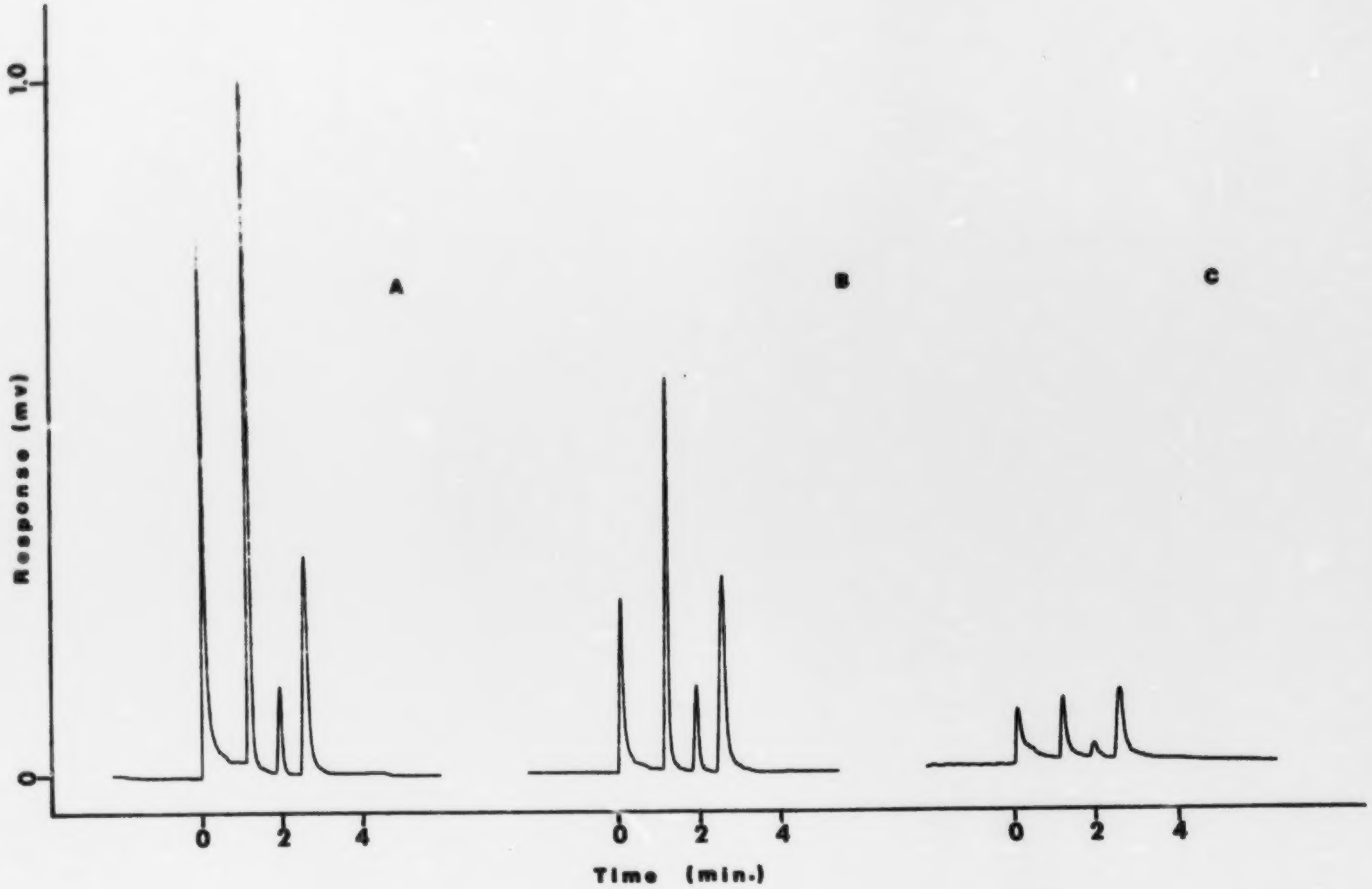

Figure 7. Chromatograms of the selectivity mixture with different conductivity solvents. Conditions: furnace temperature, 1100°; $H_2$ reaction gas, 5 cc/min; conductivity solvent, A = methyl alcohol, B = ethyl alcohol, C = isopropyl alcohol; attenuation, 3 X 1.6.

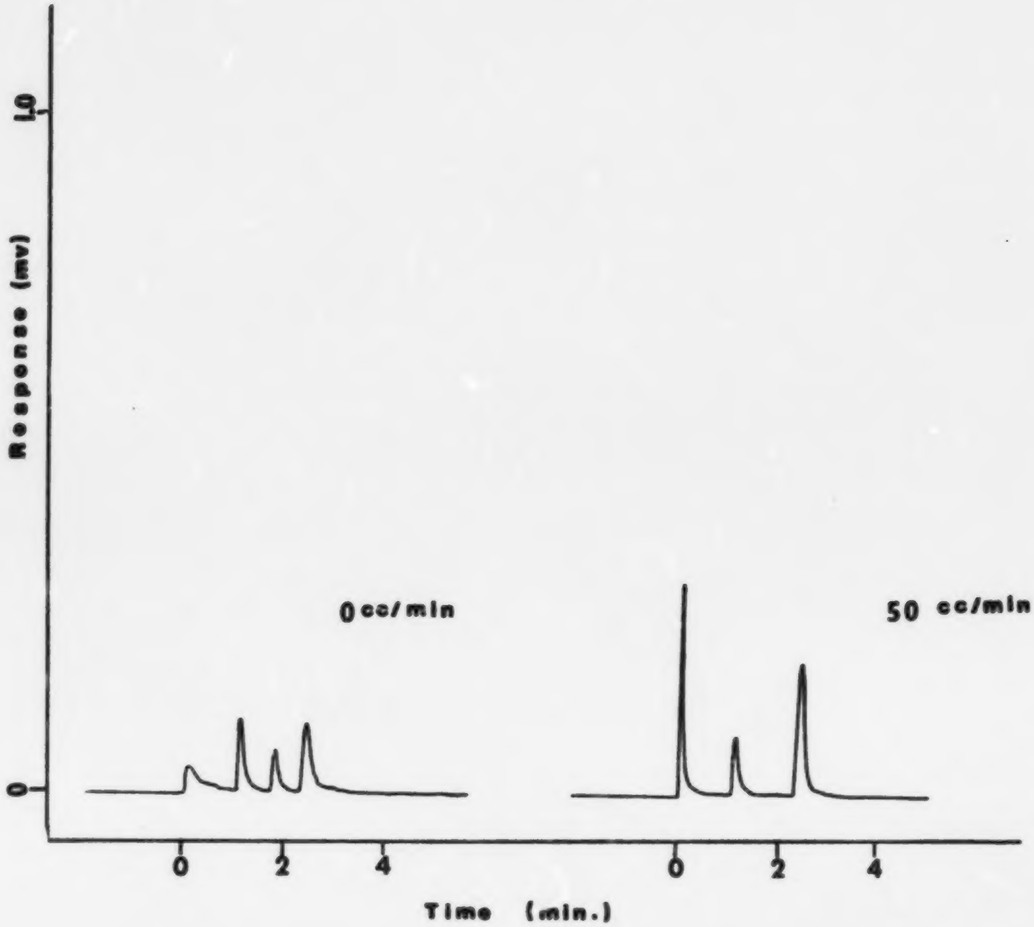

Figure 8. Chromatograms of the selectivity mixture at two different $H_2$ reaction gas flow rates. Conditions: furnace temperature, $1100^0$; conductivity solvent, isopropyl alcohol; attenuation, 3 X 1.6.

As shown in Table IX, selectivity versus parathion is > 835 using isopropyl alcohol as the conductivity solvent and 50 cc/min. of hydrogen reaction gas. Selectivity against caffeine, however, is still fairly low.

Although the selectivity and peak shape for heptachlor epoxide (See Figure 8) are quite good at a furnace temperature of $1100^{0}$ and 50 cc/min. of hydrogen reaction gas, the useful life of the quartz reaction tube is only a few days. Thus, the use of elevated temperatures to gain selectivity is not a practical solution. The upper temperature limit for the quartz tubing appears to be 900 to $950^{0}$. However, even at this temperature the quartz tube may require frequent cleaning and conditioning.

The quartz tube can be cleaned by soaking in concentrated hydrofluoric acid (48%) for approximately 5 min. and rinsing thoroughly with distilled water, methyl alcohol, acetone and hexane. After drying the tube is then treated with Sylon CT (Supelco, Inc.) for approximately 15 min. and then throughly rinsed with dry toluene followed by methyl alcohol. After this treatment the quartz tubing should be deactivated, and chromatograms with little tailing, similar to that shown in Figure 9, should be readily obtained.

"Reduction of Peak Tailing". Peak tailing is often encountered in the determination of quantities of chlorine-containing compounds of approximately 10 ng and below. Tailing peaks usually results in poor sensitivity, linearity and resolution. Thus, it is important that tailing be minimized. Tailing is usually due to the quartz reaction tube, a dirty Teflon transfer line from the furnace to the conductivity cell, a dirty conductivity cell or bleed from the ion exchange resin.

Cleaning the quartz reaction tube with hydrofluoric acid and deactivating it with Sylon CT as described above usually eliminates most of the tailing

Table IX. Influence of Hydrogen Reaction Gas Flow Rate on Specificity of Response to Heptachlor Epoxide Relative to Various Compounds in the Pyrolytic Mode Using a Furnace Temperature of 1100°C and Isopropyl Alcohol as the Conductivity Solvent.

| $H_2$ (cc/min) | Selectivity[a] | | | |
|---|---|---|---|---|
| | $n\text{-}C_{16}H_{34}$ | Caffeine | Parathion | Ethyl Stearate |
| 0 | >108,000[b] | 66 | 111 | >1,030[c] |
| 5 | >140,000 | 71 | 265 | >1,400 |
| 30 | >158,000 | 132 | >634 | >1,580 |
| 50 | >209,000 | 145 | >835 | >2,090 |

[a] Calculated from response in mho-sec/gram.

[b] Calculated using a lower value of 0.02 mho-sec/gram.

[c] Calculated using a lower value of 2 mho-sec/gram.

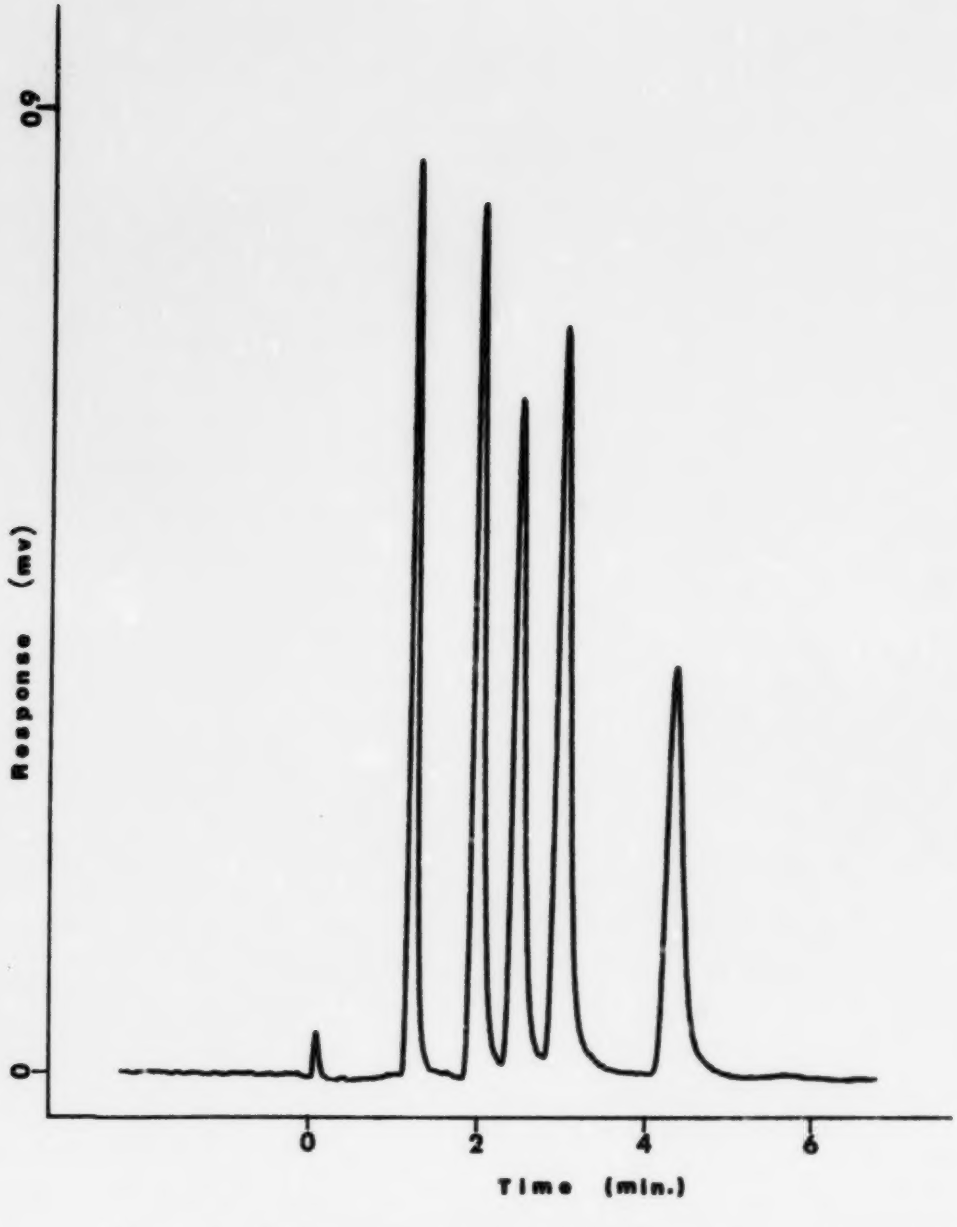

Figure 9. Chromatogram of the pesticide mixture. Conditions: furnace temperature, 800°; $H_2$ reaction gas, 5 cc/min; sample size, 10 ng; conductivity solvent, methyl alcohol; attenuation, 10 X 1.6.

associated with the tube. If tailing due to the reaction tube persists, the quartz tube should be replaced and the new tube cleaned and deactivated. The Teflon transfer line can be cleaned with organic solvents such as chloroform, acetone and hexane. The transfer line should be interfaced to the quartz reaction tube with a short piece (0.5 in.) of 1/8-in. o.d. X 1/16-in. i.d. Teflon tubing. The 1/8-in. tube is fastened to the quartz tube with a 1-in. piece of 1/8-in i.d. heat shrinkable Teflon tubing. The conductivity cell can be cleaned by disassembling and "sonicating" with 30-40% phosphoric acid, followed by distilled water, methyl alcohol, acetone and hexane. Ion exchange resin bleed can be minimized by soxhlet extracting the resin with water and then methyl alcohol for approximately 8 hr. each. Amberlite IRN-150 mixed $H^+/OH^-$ resin and Amberlite IRN-77 $H^+$ resin are the preferred resins. The ion exchange tube should be packed with 50-67% IRN-77 on the pump side and 33-50% IRN-150 on the cell side to maintain the proper acidity.

Linearity of Response to Chlorine-Containing Compounds. As shown in Figure 10, detector response to chlorine-containing compounds is linear over four to five orders of magnitude. Detector linearity in the low nanogram range (Figure 11) is very dependent upon the condition of the detector, and if peak tailing is present, response will not be linear.

Optimization of Detector Operating Conditions for the Selective Detection of Chlorinated Hydrocarbon Pesticides in the Presence of Polychlorinated Biphenyls and Polychlorinated Napthalenes. The influences of furnace temperature and hydrogen reaction gas flow rate on the response to chlorinated hydrocarbon pesticides, polychlorinated biphenyls (PCB) and polychlorinated napthalenes (PCN) were investigated using three solutions. One solution contained 10 ng per µl each of lindane heptachlor, aldrin, heptachlor epoxide and dieldrin. A second solution contained 100 ng per µl of Halowax 1013 and Aroclor 1254. A third solution contained the chlorinated pesticides and the PCB and PCN at the same concentration as

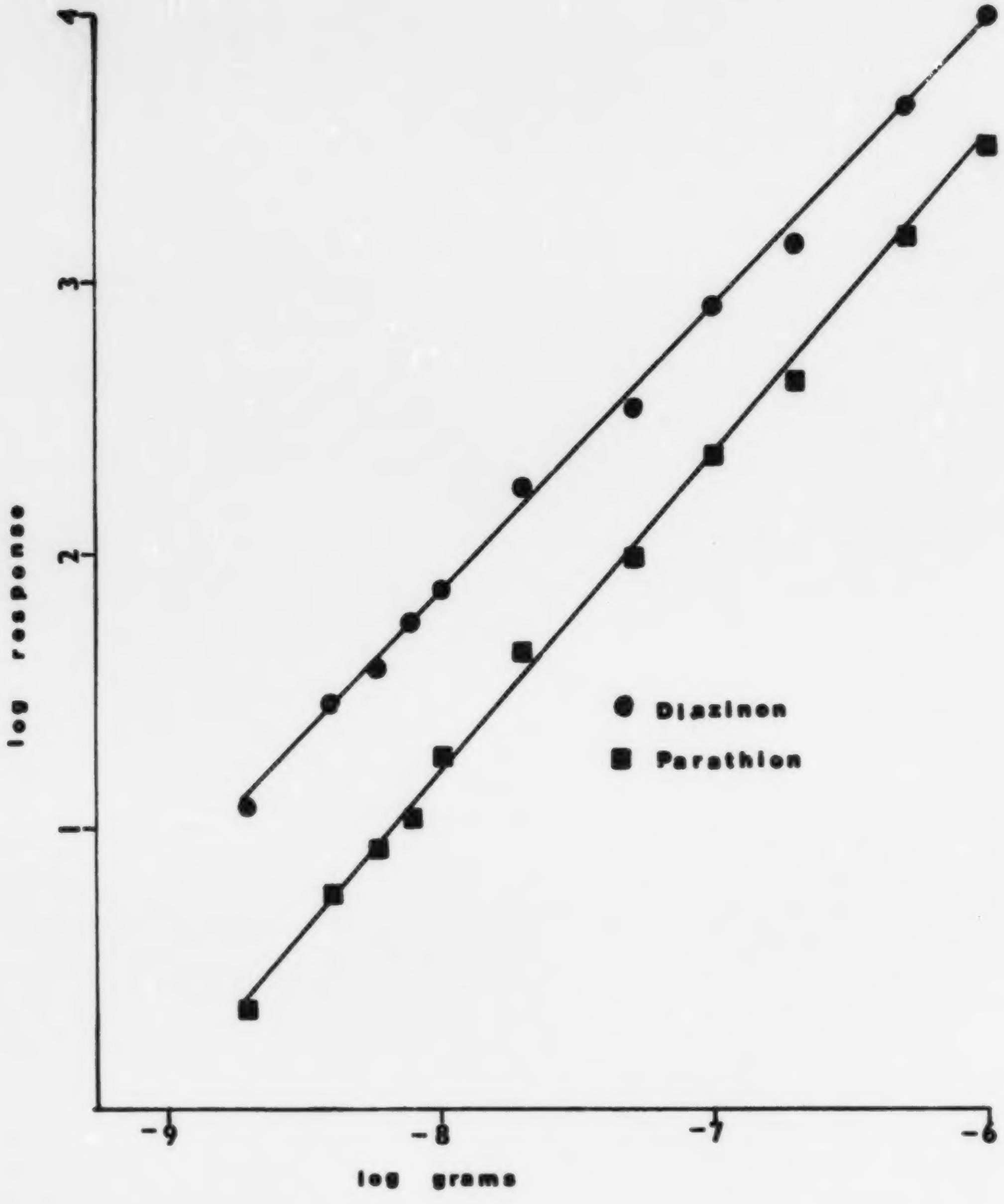

Figure 10. Linearity of response to diazinon and parathion. Conditions: furnace temperature, 700°; $H_2$ reaction gas, 0 cc/min; conductivity solvent, methyl alcohol; resin, IRN-150/77.

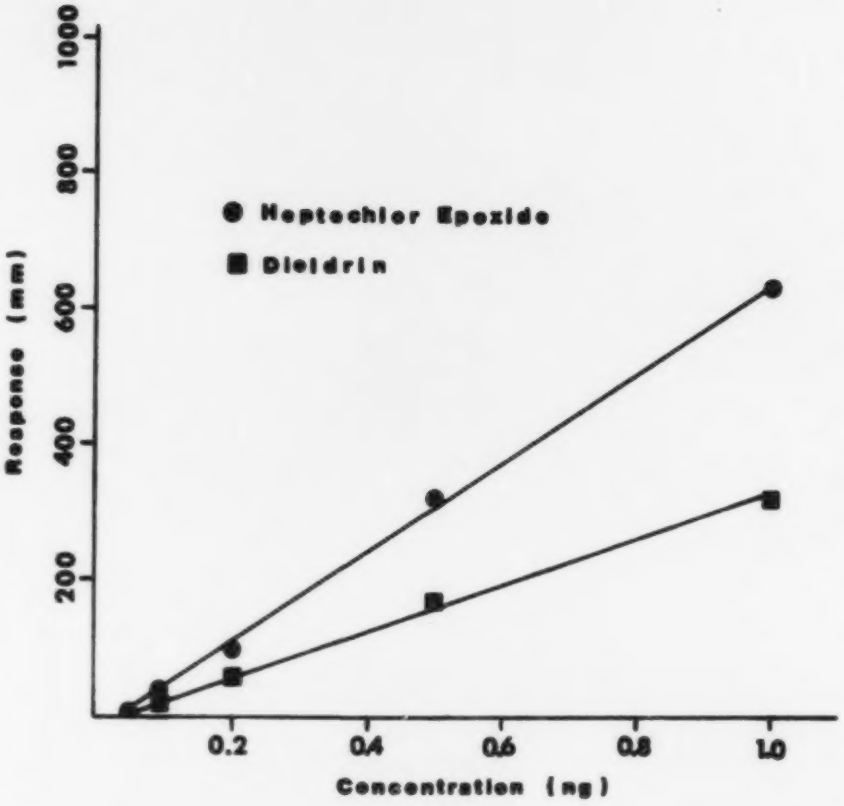

Figure 11. Linearity of response to subnanogran quantities of heptechlor epoxide and dieldrin, Conditions: furnace temperature, 700°; $H_2$ reaction gas, 10 cc/min; conductivity solvent, methyl alcohol; resin, IRN-150/77.

in the other solutions. Furnace temperature was varied from 700 to 850° in 25° increments. Hydrogen reaction gas flow rates were 0, 3 and 10 cc/min.

The results of this study are summarized in Tables X-XII. In the absence of hydrogen reaction gas, there is no response from the PCB and PCN at 800° and below. The addition of hydrogen reaction gas results in a significant increase in response to the PCB and PCN, and the furnace temperature must be 725° or below to eliminate interferences from PCB and PCN in the detection of chlorinated hydrocarbon pesticides. There appears to be little difference in the results obtained with 3 and 10 cc/min. of reaction gas. There is, however, some advantage in using reaction gas since the response to the pesticides is a little greater than without reaction gas, even at "selective" furnace temperatures. Representative chromatograms of detector response to chlorinated insecticides in the presence of PCB and PCN at a furnace temperature of 725 and 850° are shown in Figures 12 and 13, respectively.

Evaluation of Nickel Tubing for the Detection of Halogen-Containing Compounds in the Catalytic Reductive Mode. As previously discussed, specificity to halogen compounds in the pyrolytic mode is very dependent on detector operating conditions. However, conditions which give stable detector performance result in selectivities against certain compounds that may be insufficient for some analyses. Consequently, the catalytic reductive mode was investigated in an attempt to improve selectivity to halogen-containing compounds.

In the catalytic reductive mode, reaction products from organic compounds containing halogen, nitrogen, sulfur and oxygen are HX, $NH_3$, $H_2S$, $H_2O$, $CH_4$ and lower alkanes. Although $H_2O$, $CH_4$ and lower alkanes will not give a response, $NH_3$ and $H_2S$ can give significant responses unless their ionization is precluded. Since $NH_3$ is a weak base and $H_2S$ is a weak acid, their ionization can be leveled by the proper choice of conductivity solvent.

Table X. Influence of Furnace Temperature on the Response to Chlorinated Pesticides, PCB and PCN Using no Hydrogen Reaction Gas[a].

| | Furnace Temperature (°C) | | | | | | |
|---|---|---|---|---|---|---|---|
| Compound[b] | 700 | 725 | 750 | 775 | 800 | 825 | 850 |
| Lindane | 40 | 51 | 76 | 71 | 65 | 73 | 70 |
| Heptachlor | 16 | 17 | 28 | 33 | 39 | 56 | 59 |
| Aldrin | 14 | 15 | 20 | 22 | 27 | 40 | 46 |
| Hept. Epox. | 23 | 21 | 28 | 27 | 30 | 38 | 40 |
| Dieldrin | 15 | 15 | 19 | 19 | 19 | 24 | 22 |
| PCB + PCN[c] | | | | | | | |
| Peak A | ND[d] | ND | ND | ND | ND | ND | ND |
| Peak B | ND | ND | ND | ND | ND | ND | ND |
| Peak C | ND | ND | ND | ND | ND | 2 | 5 |
| Peak D | ND | ND | ND | ND | ND | ND | 2 |
| Peak E | ND | ND | ND | ND | ND | 2 | 3 |
| Lindane + Peak A | 39 | 62 | 67 | 67 | 74 | 77 | 60 |
| Heptachlor + Peak B | 16 | 23 | 25 | 32 | 45 | 59 | 56 |
| Aldrin + Peak C | 12 | 17 | 17 | 20 | 30 | 42 | 43 |
| Hept. Epox. + Peak D | 22 | 25 | 24 | 25 | 32 | 38 | 37 |
| Dieldrin + Peak E | 14 | 18 | 17 | 18 | 24 | 26 | 24 |

[a] Response is in mm of peak height.

[b] Quantity is 10 ng for each pesticide and 100 ng for PCB and 100 ng for PCN.

[c] Peaks A-E are the detector responses at retention times equal to lindane-dieldrin, respectively

[d] ND = No response detected.

Table XI. Influence of Furnace Temperature on the Response to Chlorinated Pesticides, PCB and PCN Using 3 cc/min Hydrogen Reaction Gas[a].

| Compound[b] | Furnace Temperature (°C) | | | | | | |
|---|---|---|---|---|---|---|---|
| | 700 | 725 | 750 | 775 | 800 | 825 | 850 |
| Lindane | 42 | 66 | 86 | 82 | 89 | 96 | 94 |
| Heptachlor | 52 | 64 | 98 | 104 | 104 | 99 | 76 |
| Aldrin | 28 | 32 | 58 | 75 | 85 | 82 | 65 |
| Hept. Epox. | 52 | 58 | 83 | 72 | 80 | 77 | 61 |
| Dieldrin | 27 | 31 | 48 | 43 | 47 | 46 | 32 |
| PCB + PCN[c] | | | | | | | |
| Peak A | ND[d] | ND | 1 | 5 | 11 | 22 | 25 |
| Peak B | ND | ND | ND | 40 | 46 | 50 | 38 |
| Peak C | ND | ND | 7 | 57 | 64 | 73 | 55 |
| Peak D | ND | ND | 1 | 50 | 62 | 67 | 50 |
| Peak E | ND | ND | 7 | 68 | 84 | 90 | 60 |
| Lindane + Peak A | 46 | 61 | 83 | 89 | 104 | 108 | 128 |
| Heptachlor + Peak B | 59 | 62 | 91 | 131 | 142 | 131 | 123 |
| Aldrin + Peak C | 30 | 36 | 59 | 90 | 102 | 93 | 86 |
| Hept. Epox. + Peak D | 54 | 56 | 78 | 107 | 114 | 101 | 93 |
| Dieldrin + Peak E | 32 | 34 | 66 | 119 | 119 | 115 | 108 |

[a] Response is in mm. of peak height.

[b] Quantity is 10 ng for each pesticide and 100 ng for PCB and 100 ng for PCN.

[c] Peaks A-E are the detector responses at retention times equal to lindane-dieldrin, respectively.

[d] ND = No response detected.

Table XII. Influence of Furnace Temperature on the Response to Chlorinated Pesticides, PCB and PCN Using 10 cc/min Hydrogen Reaction Gas[a].

| Compound[b] | Furnace Temperature (°C) | | | | | | |
|---|---|---|---|---|---|---|---|
| | 700 | 725 | 750 | 775 | 800 | 825 | 850 |
| Lindane | 37 | 74 | 71 | 92 | 94 | 104 | 123 |
| Heptachlor | 40 | 85 | 89 | 107 | 98 | 87 | 89 |
| Aldrin | 23 | 45 | 52 | 65 | 78 | 70 | 71 |
| Hept. Epox. | 39 | 71 | 73 | 79 | 69 | 60 | 65 |
| Dieldrin | 21 | 38 | 41 | 44 | 43 | 37 | 38 |
| PCB + PCN[c] | | | | | | | |
| Peak A | ND[d] | ND | ND | 2 | 19 | 34 | 43 |
| Peak B | ND | ND | 2 | ND | 46 | 72 | 91 |
| Peak C | ND | ND | ND | 5 | 75 | 90 | 85 |
| Peak D | ND | ND | ND | ND | 47 | 75 | 71 |
| Peak E | ND | ND | ND | 4 | 66 | 101 | 90 |
| Lindane + Peak A | 36 | 80 | 82 | 94 | 119 | 142 | 169 |
| Heptachlor + Peak B | 37 | 89 | 106 | 115 | 160 | 150 | 161 |
| Aldrin + Peak C | 26 | 50 | 65 | 74 | 131 | 123 | 133 |
| Hept. Epox. + Peak D | 34 | 71 | 83 | 82 | 130 | 126 | 134 |
| Dieldrin + Peak E | 19 | 46 | 56 | 55 | 134 | 122 | 132 |

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[a] Response is in mm. of peak height.

[b] Quantity is 10 ng for each pesticide and 100 ng for PCB and 100 ng for PCN.

[c] Peaks A-E are the detector responses at retention times equal to lindane-dieldrin, respectively.

[d] ND = No response detected.

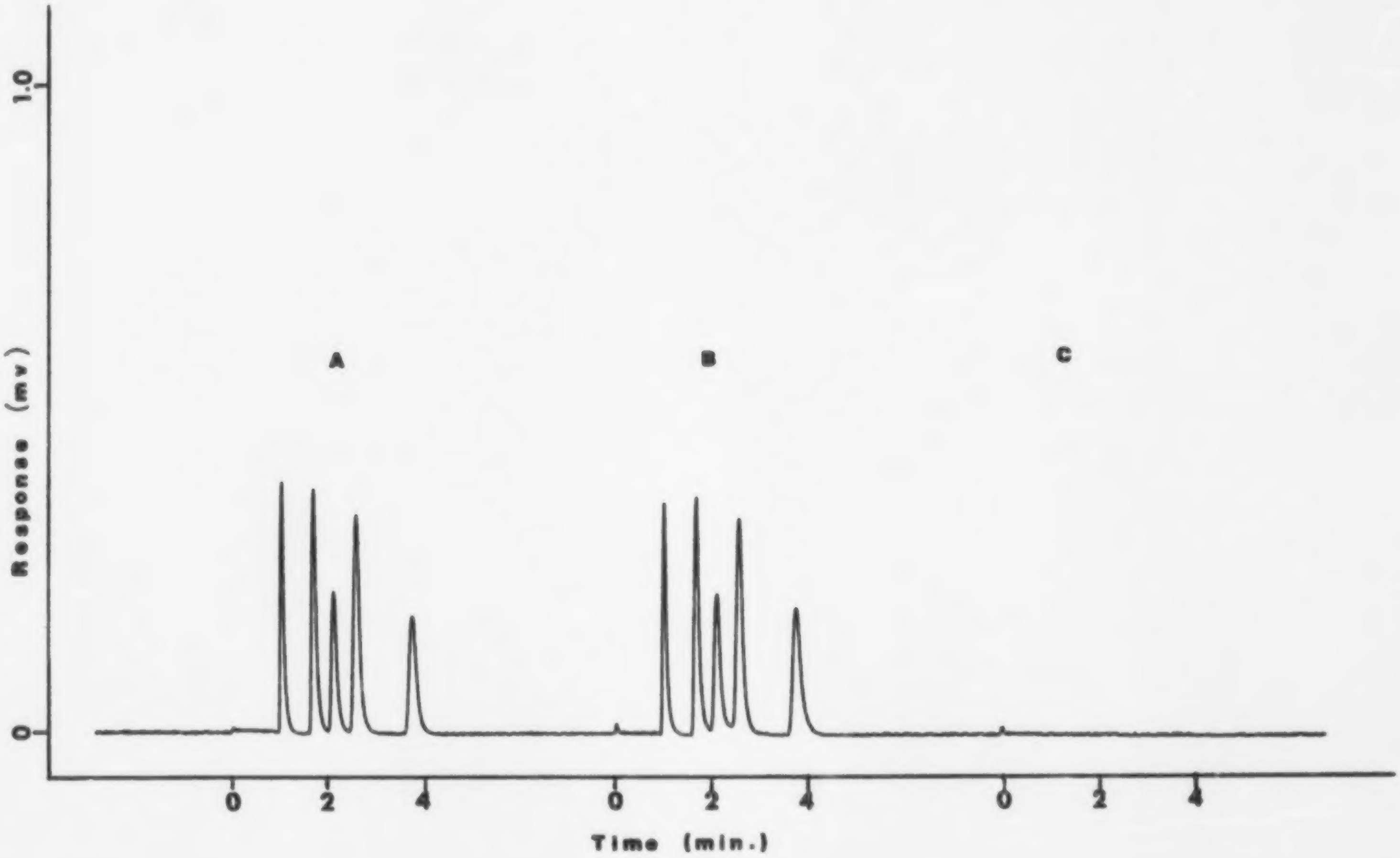

Figure 12. Chromatograms of the chlorinated pesticide mixture in the presence of PCB and PCN. Conditions: furnace temperature, 725°; $H_2$ reaction gas, 3 cc/min; conductivity solvent, methyl alcohol; A, 10 ng of chlorinated pesticides; B, A + 100 ng PCB + 100 ng PCN; C, 100 ng of PCB and 100 ng PCN.

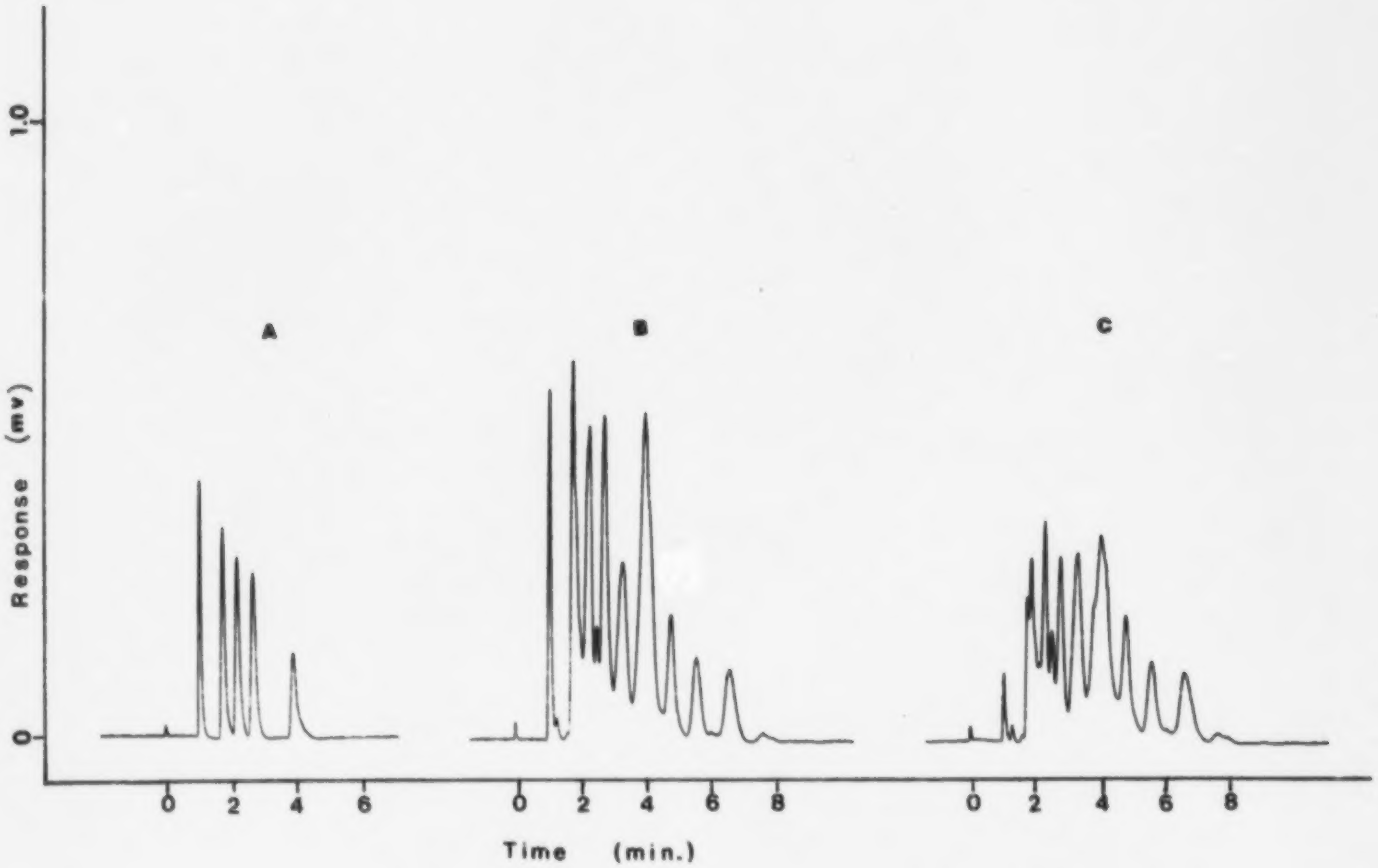

Figure 13. Chromatograms of the chlorinated pesticide mixture in the presence of PCB and PCN. Conditions: furnace temperature, 850$^o$; $H_2$ reaction gas, 3 cc/min; conductivity solvent, methyl alcohol; A, 10 ng of the pesticide mixture; B, A + 100 ng PCB + 100 ng PCN; C, 100 ng PCB and 100 ng PCN.

Nickel tubing was chosen instead of a quartz tube packed with a nickel catalyst because it will not break and is free of polar absorption sites. Nickel tubing 1/8 in. o.d. X 0.08 in. i.d. and 1/16 in. o.d. X 0.02 in. i.d. were evaluated. The large tubing did not give adequate reduction, but the small tubing was very effective.

The influences of furnace temperature, hydrogen reaction gas flow rate and conductivity solvent on detector sensitivity, linearity and selectivity to halogen-containing compounds were investigated using a 1/16-in. o.d. X 0.02-in. i.d. X 5.0-in. nickel reaction tube. A 1/8-in. to 1/16-in. Vespel reducing ferrule was used to connect the reaction tube to the furnace, and the Teflon transfer tube was connected to the reaction tube with a 3/16-in. o.d. X 1/16-in. i.d. X 3/8-in. Vespel tube.

As shown in Figure 14, detector response to the selectivity mixture is fairly independent of furnace temperature over a range of approximately $100^{o}$. This indicates that the nickel reaction tube gives complete reduction of the compounds from 850 to $950^{o}$. It can also be seen that there is no response from ethyl stearate, which indicates that the ester function has been effectively reduced. Although there is no response to hexadecane and ethyl stearate with methyl alcohol as the conductivity solvent, response is greater for caffeine than that obtained using quartz tubing, and response to parathion is approximately the same.

In contrast to quartz tubing, however, the response to non-halogen compounds can be greatly reduced by using a longer chained alcohol as the conductivity solvent. The influence of conductivity solvent on response to the selectivity mixture is shown in Figure 15. As can be seen in this figure, the use of ethyl alcohol results in small negative responses for caffeine and parathion instead of the large positive responses observed with methyl alcohol. The degree of the

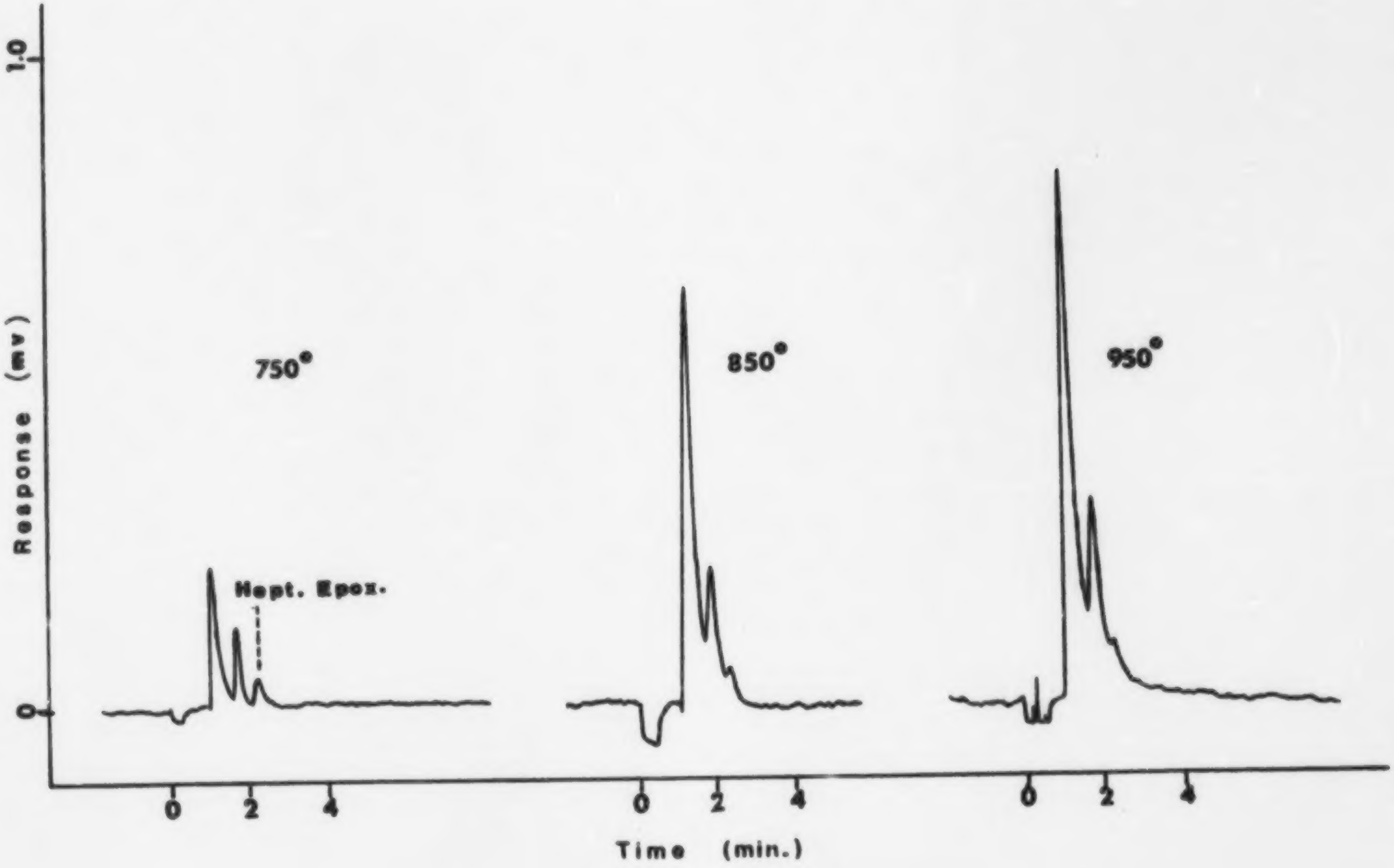

Figure 14. Chromatograms of the selectivity mixture with a nickel reaction tube at different furnace temperatures. Conditions: $H_2$ reaction gas, 80 cc/min; conductivity solvent, methyl alcohol; attenuation, 1 X 6.4.

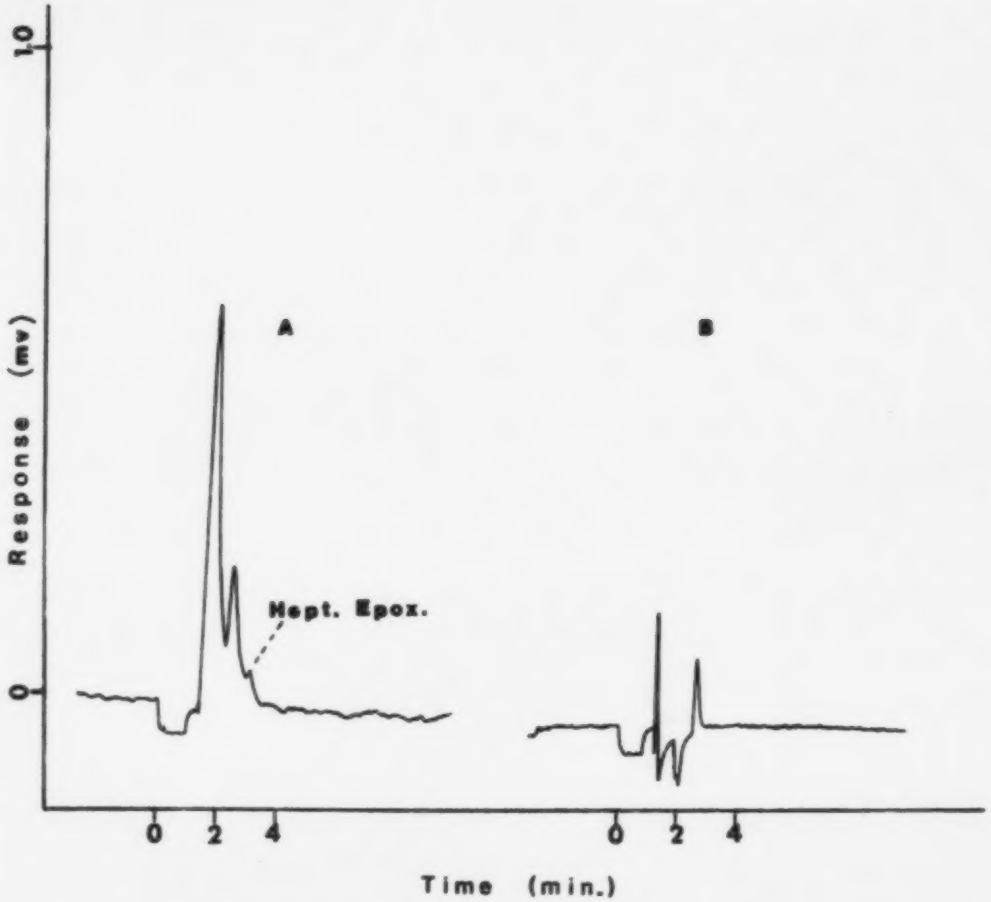

Figure 15. Chromatograms of the selectivity mixture with a nickel reaction tube and different conductivity solvents. Conditions: furnace temperature, 850°; $H_2$ reaction gas 100 cc/min; conductivity solvent; A = methyl alcohol, B = n-butyl alcohol; attenuation, A = 1 X 6.4, B = 1 X 1.6.

negative response is decreased by the use of n-propyl alcohol and essentially eliminated with n-butyl alcohol.

The negative response for nitrogen-containing compounds is a result of decreasing the conductivity of the solvent by replacing the larger specific conductance of the proton with that of the ammonium ion. Consequently, the degree of negative response will depend upon the amount of bleed from the ion exchange resin ($H^+$ form), the quantity of ammonia produced and the ionizing properties of the conductivity solvent. The degree of negative response should decrease with time since ion exchange resin bleed decreases.

The effect of reaction conditions on detector sensitivity and specificity to chlorine-containing compounds is shown in Tables XIII and XIV. Detector response (with 40 cc/min helium carrier gas) increases with hydrogen reaction gas flow rate up to 60 cc/min. Response is approximately the same for flow rates of 60 and 100 cc/min. (Table XIII).

Detector specificity to chlorine containing compounds versus nitrogen-, sulfur- and ester-containing compounds as a function of furnace temperature was determined with m-chlorotoluene (10 ng), m-tolunitrile (10 μg), thioanisole (10 μg) and methyl o-toluate (10 μg). Detector selectivity for chlorine versus nitrogen increases with furnace temperature from 800 to 900°, and reaches a value of 4,300 at 900° (See Table XIV). However, selectivity to chlorine versus sulfur or esters reaches a maximum at 870°, and is 9,500 and 95,600 against sulfur and esters, respectively.

The influence of furnace temperature and conductivity solvent on the response to non-halogen compounds was also investigated using the selectivity mixture employed in the pyrolytic mode studies. The results of this study are summarized in Table XV. As indicated by Figure 15, selectivity for heptachlor epoxide versus caffeine and parathion is very poor with methyl alcohol as the conductivity solvent, but is good with n-butyl alcohol.

Table XIII. Influence of Hydrogen Reaction Gas Flow Rate on Detector Response to Chlorinated pesticides in the Catalytic Reductive Mode with a Nickel Reaction Tube[a,b].

| | Peak Height (mm) | | | | |
|---|---|---|---|---|---|
| Flow Rate (cc/min) | Lindane | Hept. | Aldrin | Hept. Epox. | Dieldrin |
| 20 | 39 | 42 | 32 | 28 | 17 |
| 30 | 50 | 55 | 39 | 38 | 20 |
| 60 | 76 | 53 | 40 | 39 | 22 |
| 100 | 78 | 50 | 40 | 36 | 23 |

[a] Furnace temperature was 840°; conductivity solvent was n-butyl alcohol.

[b] Sample size was 1 ng.

Table XIV. Influence of Furnace Temperature on Detector Specificity to Chlorine Relative to Nitrogen, Sulfur and Esters in the Catalytic Reductive Mode with a Nickel Reaction Tube[a,b]

| Furnace Temperature | Element | | |
|---|---|---|---|
| | N | S | $-O-\underset{\vert}{C}=O$ |
| 800 | 1,920 | 9,870 | 32,020 |
| 870 | 3,360 | 9,500 | 95,600 |
| 900 | 4,300 | 5,020 | 42,400 |

[a] Reaction gas flow rate was 100 cc/min of hydrogen; conductivity solvent was *n*-butyl alcohol.

[b] Selectivities were calculated from peak areas using *m*-chlorotoluene (10 ng), *m*-tolunitrile (10 μg), thioanisole (10 μg) and methyl *o*-toluate (10 μg).

Table XV. Influence of Conductivity Solvent and Furnace Temperature on Selectivity to Chlorine in the Catalytic Reductive Mode[a].

| Conductivity Solvent | Furnace Temperature | Selectivity | | | |
|---|---|---|---|---|---|
| | | $n$-$C_{16}$ | Caffeine | Parathion | Ethyl Myristate |
| MeOH | 700 | ND[b] | 6 | 11 | ND |
| | 750 | ND | 8 | 20 | ND |
| | 800 | ND | 4 | 36 | ND |
| | 850 | ND | 1 | 8 | ND |
| | 900 | ND | 1 | 4 | ND |
| | 950 | ND | 1 | 4 | ND |
| EtOH | 700 | ND | 8 | 17 | ND |
| | 750 | ND | 188 | 57 | ND |
| | 800 | ND | NR[c] | 2,225 | ND |
| | 850 | ND | NR | NR | ND |
| | 900 | ND | NR | NR | ND |
| | 950 | ND | NR | NR | ND |
| n-PrOH | 800 | ND | NR | NR | ND |
| | 850 | ND | NR | NR | ND |
| | 900 | ND | 247 | NR | ND |
| | 950 | ND | 288 | NR | ND |
| n-BuOH | 750 | ND | NR | NR | ND |
| | 800 | ND | NR | NR | ND |
| | 850 | ND | NR | NR | ND |
| | 900 | ND | NR | NR | ND |
| | 950 | ND | NR | NR | ND |

[a] Hydrogen reaction gas flow rate was 100 cc/min.

[b] ND = No response detected.

[c] NR = Negative response.

Linearity of detector response to chlorine-containing pesticides with a nickel reaction tube is shown in Figure 16. Response is linear from 0.1 ng to 1 µg. Linearity of response for sample quantities below apprixmately 25 ng depends upon the condition of the nickel tube. New tubes must be conditioned for several days before they exhibit good linearity and peak shape, but once conditioned last for six months or more. Contaminants in the helium carrier gas also contribute to non-linear response and poor peak shape. Contamination was present in approximately two out of every three tanks of helium, and for this reason electrolytic hydrogen was used for both the carrier and reaction gas for most applications.

Minimum Detectable Quantity. The minimum detectable quantity, defined as that quantity of material required to give a response twice that of background, depends upon the same factors that influence peak shape and linearity. It also depends upon furnace temperature and conductivity solvent. Although detector response is greater for aqueous conductivity solvents, the signal-to-noise ratio is greater for absolute alcohols. Thus, the minimum detectable level is less for absolute alcohols than for the 1:1 isopropyl alcohol/water conductivity solvent recommended by the manufacturer. In general, minimum detectable levels of 20-50 pg are usually obtained for the common chlorinated hydrocarbon pesticides at retention times of five minutes or less. The minimum detectable quantities for representative chlorinated pesticides analyzed at different operating conditions are listed in Table XVI. Representative chromatograms of low levels of pesticides are displayed in Figure 17.

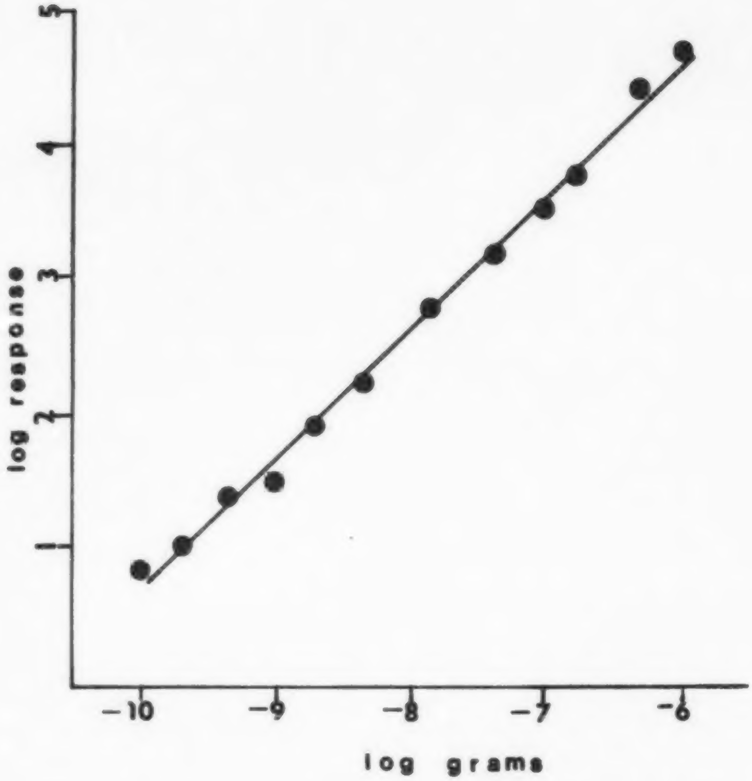

Figure 16. Linearity of response to lindane with a nickel reaction tube. Conditions: furnace temperature, 840°; $H_2$ reaction gas, 100 cc/min; conductivity solvent, methyl alcohol; resin, IRN-150/77.

Table XVI. Minimum Detectable Quantities of Halogen-Containing Compounds[a].

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| Conditions | Compound<br>Lindane | <br>Heptachlor | <br>Aldrin | <br>Hept. Epox. | <br>Dieldrin |
|---|---|---|---|---|---|
| Nitrobenzene<br>2/3 IRN-150 + 1/3 IRN-77<br>FT = 950°, $H_2$ = 5 cc<br>2 mm id. quartz tube | 14pg<br>(0.88)[b] | 17pg<br>(1.48) | 19pg<br>(1.84) | 11pg<br>(2.24) | 13<br>(3.20) |
| 25% Isopropyl alcohol<br>IRN-150<br>FT = 850°, $H_2$ = 3 cc<br>2 mm id. quartz tube | 17pg<br>(1.04) | 25pg<br>(1.76) | 33pg<br>(2.24) | 33pg<br>(2.72) | 40pg<br>(4.00) |
| Methyl alcohol<br>2/3 IRN-150 + 1/3 IRN-77<br>FT = 700°, $H_2$ - 10 cc<br>2 mm i.d. quartz tube | 22pg<br>(0.80) | 25pg<br>(1.32) | 33pg<br>(1.60) | 29pg<br>(1.96) | 44pg<br>(2.80) |
| Methyl alcohol<br>2/3 IRN-150 + 1/3 IRN-77<br>FT = 860°, $H_2$ = 140 cc<br>Nickel tube | 11pg<br>(1.04) | 17pg<br>(1.64) | 17pg<br>(2.08) | 18pg<br>(2.52) | 27pg<br>(3.64) |
| n-Butyl alcohol<br>2/3 IRN-150 + 1/3 IRN-77<br>FT - 860°, $H_2$ = 140 cc<br>Nickel tube | 63pg<br>(1.12) | 83pg<br>(1.88) | 100pg<br>(2.32) | 83pg<br>(2.80) | 111<br>(4.08) |

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[a] Minimum detectable quantities are that 2x noise and short-term drift.

[b] Values in parenthesis are retention times in minutes.

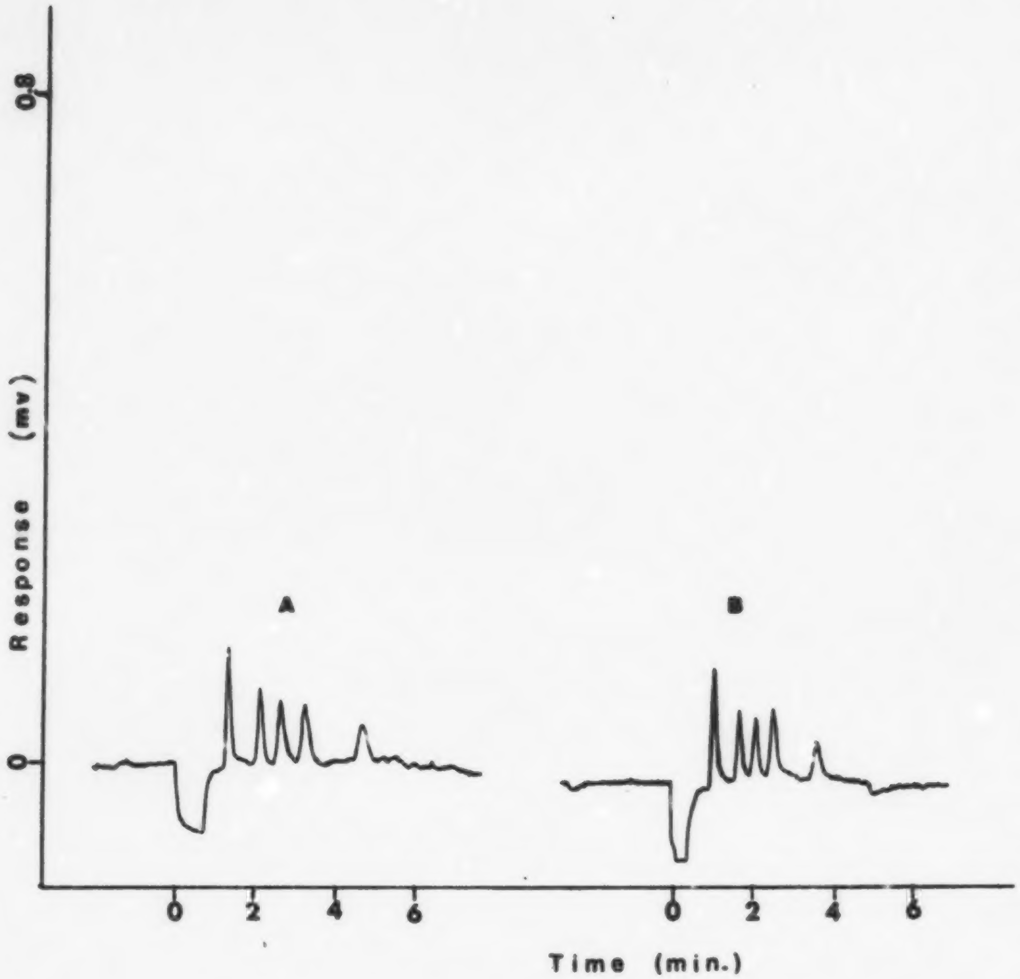


Figure 17. Chromatograms of low levels of the chlorinated pesticide mixture with a nickel reaction tube. Conditions: furnace temperature, 850°; $H_2$ reaction gas, 100 cc/min; conductivity solvent, methyl alcohol; sample quantity, A = 0.1 ng of each compound, B = 0.25 ng of each compound; attenuation, A = 1 X 0.2, B = 1 X 0.4.

## Detection of Sulfur-Containing Compounds

Optimization of Detector Operating Conditions. Sulfur-containing compounds are detected as the strong acids $H_2SO_3$ and $H_2SO_4$ which are formed from the combustion products $SO_2$ and $SO_3$. Organic sulfur-containing compounds can be converted to $SO_2$ and $SO_3$ by oxidative pyrolysis or catalytic oxidation. The formation of $SO_3$ is favored at moderate furnace temperatures, whereas $SO_2$ is favored at higher temperatures. However, since both $SO_2$ and $SO_3$ are converted to the strong acids $H_2SO_3$ and $H_2SO_4$ upon contact with water, the relative quantities of these sulfur species is of little importance. Quartz reaction tubes are used for the pyrolytic oxidation of sulfur compounds, and either nickel reaction tubes or quartz tubes with an oxidation catalyst are used for the catalytic oxidation mode. Oxygen or air can be used for the reaction gas.

"Conductivity Solvent and Reaction Systems." Detector sensitivity and specificity to sulfur-containing compounds are dramatically influenced by contact material (or catalyst), type and pH of the conductivity solvent, and reaction gas flow rate. The specific detection of sulfur compounds is complicated by interferences from all carbon-containing compounds since the detection of organic carbon has the same general requirements as the detection of sulfur. In the oxidative mode, organic carbon is converted to $CO_2$ and upon contact with water $CO_2$ forms the weak acid $H_2CO_3$. Thus, optimization of detector operating conditions are extremely important, and the greater ease of oxidation of sulfur compounds and the strong acidity of $H_2SO_3$ and $H_2SO_4$ must be taken to full advantage.

The influence of detector operating conditions was investigated using diazinon and parathion as probe sulfur compounds. Specificity to sulfur was determined relative to hydrocarbons (n-hexadecane) and esters (ethyl myristate) as the response in peak height per gram of sulfur divided by the response in peak height per gram of hydrocarbon or ester.

The influence of furnace temperature on detector specificity was studied from 600 to 950$^0$ using 1-mm and 2-mm i.d. quartz reaction tubes with and without contact materials. In general, there was little difference in specificity between the two sizes of tubes. However, the small i.d. tube was very resistant to contamination, whereas the larger tube exhibited a slight tendency to become contaminated when operated at the lower furnace temperatures. Platinum wire, copper wire, nickel wire, gold wire, Nichrome wire, Chromosorb W, quartz chips and quartz wool were evaluated as contact materials.

The influence of furnace temperature on detector response to sulfur-containing pesticides depends upon whether an empty quartz tube or a quartz tube with a contact material is used. In general, response increases with furnace temperature up to a given temperature, and may in some instances reach a plateau or decrease with a further increase in temperature (See Tables XVII and XVIII). With an empty quartz reaction tube, response usually continues to increase with furnace temperature over the range 700 to 950$^0$ with conductivity solvents containing a considerable quantity of water (compare 50 and 100% isopropyl alcohol in Table XVII). However, if the conductivity solvent does not contain sufficient water, response usually reaches a maximum at 850 to 900$^0$. This response-temperature relationship is also observed for quartz reaction tubes containing a quartz wool contact material. However, as shown in Figure 18, response with a quartz wool contact material is a complex function of furnace temperature. Response with a platinum catalyst reaches a maximum at approximately 700$^0$ and decreases with a further increase in temperature (See Table XVIII).

Table XVII. Influence of Furnace Temperature on Detector Response to Sulfur Compounds Using an Empty Quartz Reaction Tube and Various Conductivity Solvents[a,b].

| Conductivity Solvent | Compound | Furnace Temperature (°C) 700 | 750 | 800 | 850 | 900 | 950 |
|---|---|---|---|---|---|---|---|
| 25% *i*-PrOH | diazinon | 10 | 14 | 19 | 27 | 35 | 40 |
| | parathion | 10 | 13 | 15 | 17 | 21 | 24 |
| 50% *i*-PrOH | diazinon | 10 | 26 | 55 | 80 | 99 | 102 |
| | parathion | 10 | 28 | 33 | 36 | 45 | 53 |
| 75% *i*-PrOH | diazinon | 10 | 14 | 25 | 36 | 41 | 39 |
| | parathion | 10 | 12 | 18 | 19 | 21 | 21 |
| 100% *i*-PrOH | diazinon | 10 | 13 | 18 | 21 | 21 | 19 |
| | parathion | 10 | 12 | 14 | 15 | 15 | 15 |

[a] Reaction tube was 2 mm i.d.; reaction gas = 4 cc/min $O_2$.

[b] Response = relative peak height with response at 700° assigned a value of 10.

Table XVIII. Influence of Furnace Temperature on Detector Response to Sulfur Compounds Using a Platinum Catalyst and Various Conductivity Solvents[a,b].

| Conductivity Solvent | Compound | Furnace Temperature (°C) | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | 575 | 600 | 650 | 700 | 750 | 800 | 850 | 900 |
| MeOH | diazinon | 10 | 17 | 19 | 17 | 16 | 15 | 14 | 18 |
| | parathion | 10 | 14 | 16 | 18 | 16 | 14 | 14 | 17 |
| EtOH | diazinon | 10 | 13 | 24 | 27 | 25 | 24 | 21 | 21 |
| | parathion | 10 | 13 | 19 | 23 | 22 | 23 | 21 | 21 |
| _i_-PrOH | diazinon | 10 | 12 | 18 | 19 | 17 | 17 | 14 | 14 |
| | parathion | 10 | 12 | 15 | 16 | 16 | 16 | 14 | 14 |

[a] Reaction tube was 1 mm i.d. and contained 1 cm of #35 platinum wire; reaction gas = 4 cc/min $O_2$.

[b] Response = relative peak height with response at 575 assigned a value of 10.

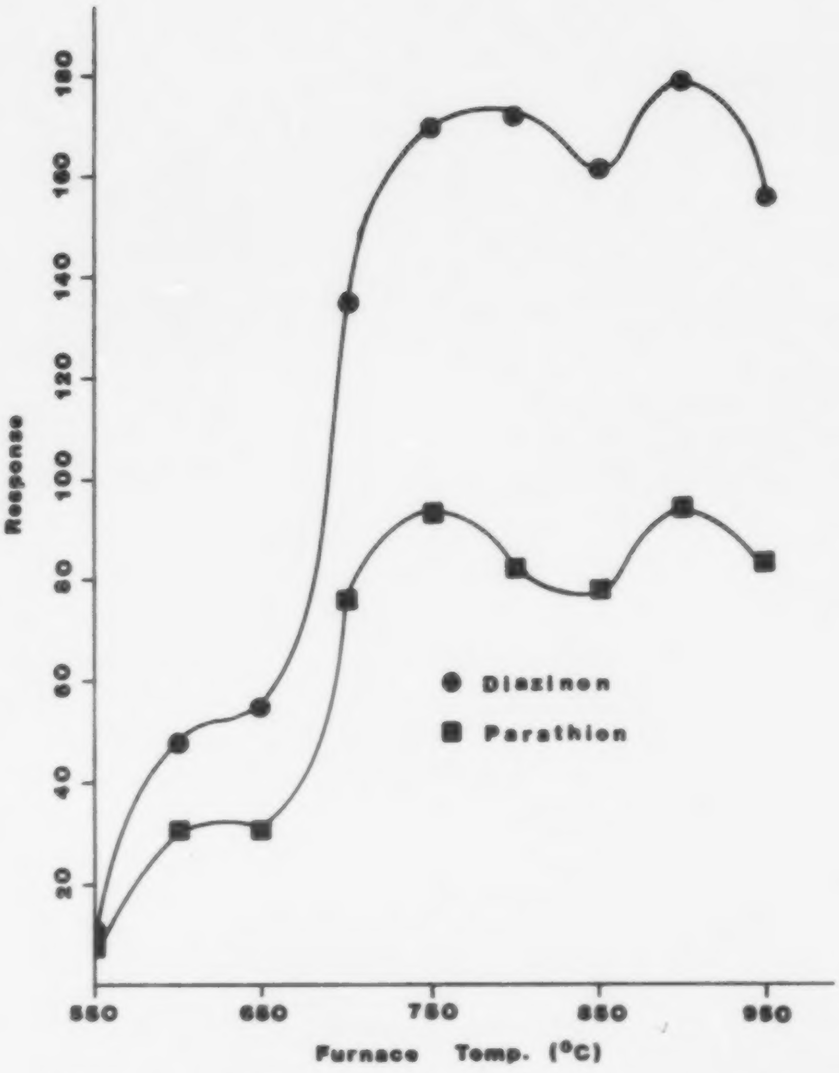


Figure 18. Detector response to diazinon and parathion as a function of furnace temperature. Conditions: 1-mm i.d. quartz reaction tube packed with 0.25 in. of quartz wool; conductivity solvent, methyl alcohol.

The decrease in response with temperature after reaching a maximum perhaps can be explained by the temperature dependence of the $SO_2$:$SO_3$ ratio and possible differences in solubilities under the conditions of operation. This relationship, however, exhibits considerable variability. It changes slightly with time and is not highly consistent with different reaction tubes. Therefore, response should be optimized periodically.

Platinum and quartz wool proved to be the only useful contact materials. The other materials investigated either resulted in poor sensitivity, peak tailing or excessive detector background noise. Detector specificity to sulfur versus hydrocarbons and esters as a function of furnace temperature for an empty reaction tube, reaction tube with quartz wool contact material and reaction tube with platinum catalyst is exhibted in Tables XIX-XXI, respectively.

As shown by the data displayed in Tables XIX-XXII, conditions for maximum selectivity do not necessarily coincide with those for maximum sensitivity. With an empty quartz reaction tube, selectivity versus hydrocarbons and esters decreases with temperature to a minimum at 800° and then increases with a further increase in temperature (See Table XIX). Selectivity relative to hydrocarbons is maximum at 700°, whereas selectivity relative to esters is maximum at 950°. Selectivity as a function of furnace temperature is similar with quartz wool as a contact material as that displayed with an empty tube (See Table XX). Again, selectivity reaches a minimum, but at a slightly lower temperature (750°), and then increases. Selectivity is also greater relative to esters than hydrocarbons at high furnace temperatures. In contrast to an empty tube, selectivity relative to esters is maximum at the low furnace temperature, as found for hydrocarbons in both cases. Selectivity with a platinum catalyst also reaches a minimum, which is at 900°. Comparison of Figures 19 and 20 demonstrate the importance of furnace temperature for extremes in operating conditions.

Table XIX. Selectivity of the HECD to Sulfur Compounds Relative to Hydrocarbons Using 75% Isopropanol as the Conductivity Solvent[a]

| | Selectivity | |
|---|---|---|
| Furnace Temperature | Hydrocarbons | Esters |
| 700 | 37,200 | 4,800 |
| 750 | 10,000 | 600 |
| 800 | 480 | 440 |
| 850 | 1,080 | 1,320 |
| 900 | 3,720 | 3,720 |
| 950 | 12,600 | 24,400 |

[a] Reaction tube was empty and 2 mm I.D.

Table XX. Influence of Furnace Temperature on the Selectivity of the HECD to Sulfur Compounds Using Quartz Wool as a Contact Material[a].

| Furnace Temperature | Selectivity<br>Hydrocarbon | <br>Ester |
|---|---|---|
| 550 | > 83,000 | > 83,000 |
| 600 | >386,000 | >386,000 |
| 650 | 436,000 | 72,600 |
| 700 | 214,450 | 57,000 |
| 750 | 56,720 | 15,810 |
| 800 | 94,600 | 24,100 |
| 850 | 40,250 | 49,500 |
| 900 | 37,700 | 62,300 |
| 950 | 23,100 | 40,250 |

[a] Reaction tube was 1 mm I.D.; Conductivity solvent was methyl alcohol.

Table XXI. Selectivity of the HECD to Sulfur Compounds Using a Platinum Catalyst and Various Concentrations of Isopropanol as the Conductivity Solvent.

| Furnace Temperature | %Isopropanol | Selectivity Hydrocarbon | Selectivity Ester |
|---|---|---|---|
| 700 | 10 | 9,200 | 7,500 |
| 750 | | 6,900 | 6,800 |
| 800 | | 2,600 | 4,480 |
| 850 | | 1,920 | 3,440 |
| 900 | | 840 | 1,020 |
| 950 | | 1,100 | 2,220 |
| 725 | 75 | 7,600 | 10,800 |
| 800 | | 6,520 | 8,400 |
| 725 | 90 | 8,200 | 12,560 |
| 800 | | 7,125 | 11,360 |
| 725 | 100 | 23,320 | 22,000 |
| 800 | | 17,200 | 15,600 |

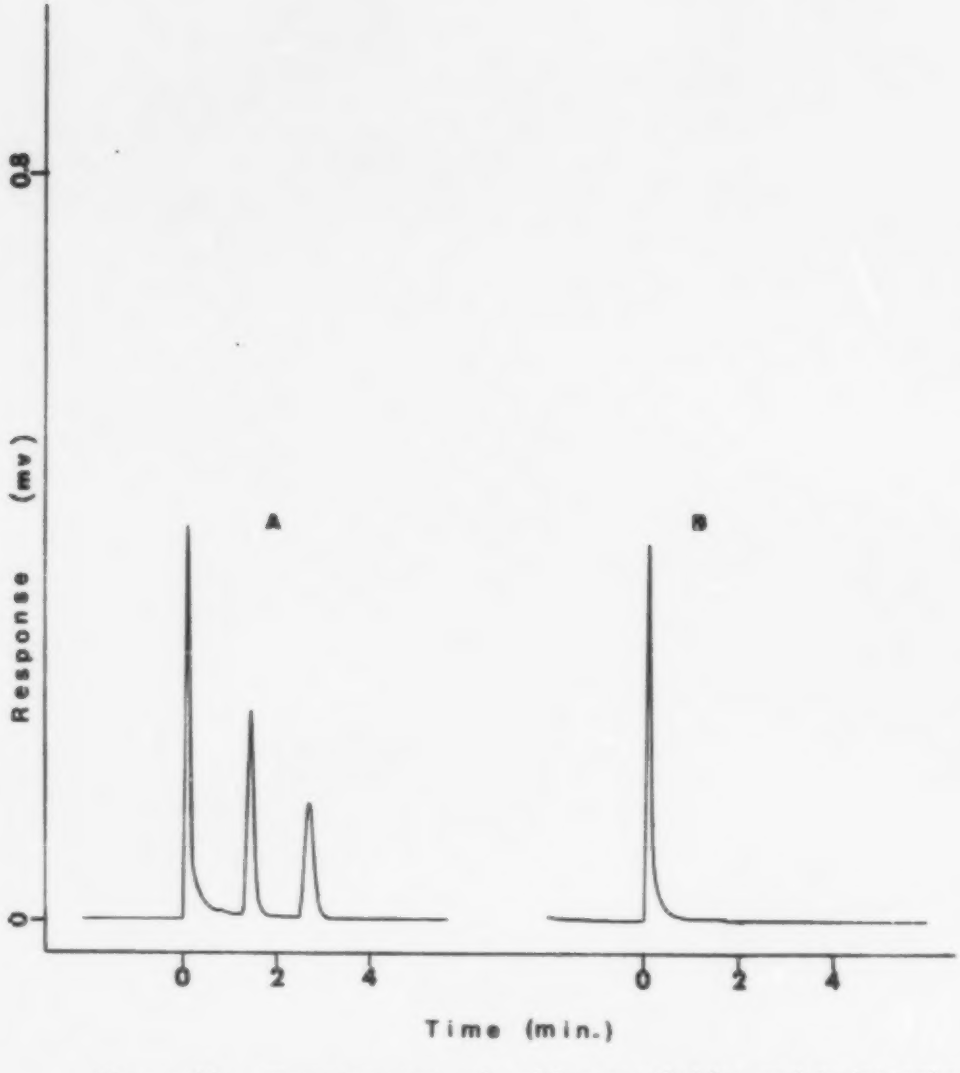


Figure 19. Chromatograms of sulfur pesticides and hydrocarbons with a quartz reaction tube packed with quartz wool. Conditions: furnace temperature, 650°; conductivity solvent, methyl alcohol; $O_2$ reaction gas, 4 cc/min; sample, A = 5 ng of diazinon and parathion, B = 2 μg of the hydrocarbons ($C_{16}$, $C_{18}$, $C_{19}$ and $C_{21}$).

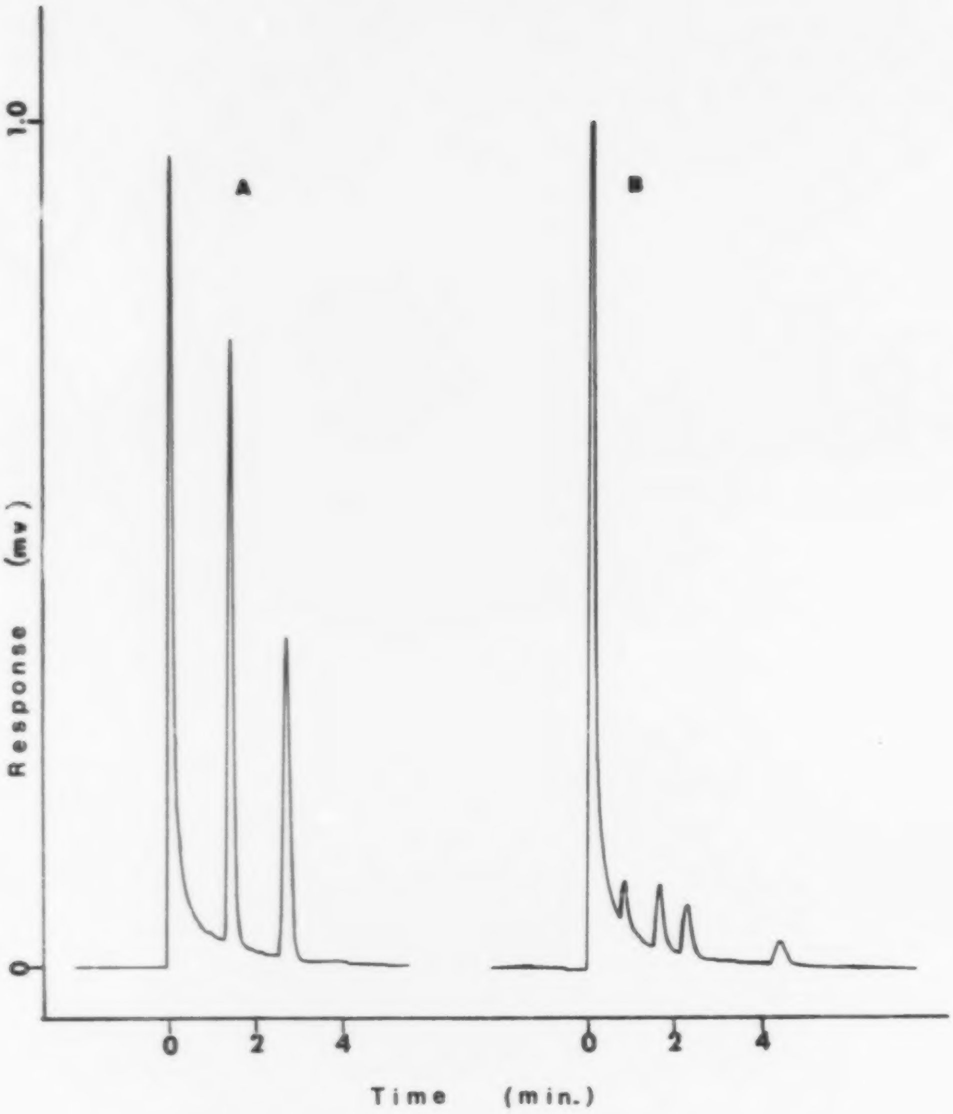


Figure 20. Chromatograms of sulfur pesticides and hydrocarbons with a quartz reaction tube packed with quartz wool. Conditions: furnace temperature, 900°; conductivity solvent, methyl alcohol; $O_2$ reaction gas, 4 cc/min; sample, A = 5 ng of diazinon and parathion, B = 2 μg of the hydrocarbons ($C_{16}$, $C_{18}$, $C_{19}$ and $C_{21}$).

The effectsof different concentrations of water in the conductivity solvent on selectivity to sulfur relative to hydrocarbons and esters using an empty quartz reaction tube and a reaction tube containing a platinum catalyst are shown in Figures 21 and 22. The presence of 25% water in the isopropyl alcohol conductivity solvent greatly decreases the selectivity obtained with an empty reaction tube. Increase in the quantity of water above 25% has little additional effect. Selectivity obtained with a platinum catalyst is also decreased by the addition of water to the conductivity solvent. The selectivity obtained with the platinum catalyst is fairly low, however; and the effect of water is not as great.

The flow rate of reaction gas is an important factor. Selectivity to sulfur relative to hydrocarbons as a function of oxygen flow rate and furnace temperature is tabulated in Table XXII. Flow rates of 2-5 cc/min. gave a large solvent response, whereas flow rates lower than approximately 2 cc/min. gave diminished response to sulfur compounds and resulted in elevated noise levels. The selectivity-furnace temperature trend, previously discussed, is slightly altered by reaction gas flow rate. With a reaction gas flow rate of 2 cc/min. selectivity is greater at 700$^{0}$ than 950$^{0}$, as is also the case for the reaction conditions described in Table XIX. This relationship is reversed at higher reaction gas flow rates.

Although the greatest selectivities to sulfur relative to hydrocarbons and esters are achieved with a 1-mm quartz reaction tube packed with approximately 0.25 in. of quartz wool, detector response and selectivity deteriorates after approximately a week of use. The same is also true for a platinum catalyst. Attempts to recondition the quartz wool and platinum catalyst by rinsing the reaction tube with organic solvents and/or hydrofluoric acid were not successful. Thus, for optimum performance the quartz wool should be replaced periodically. Since significantly higher selectivities are obtained with

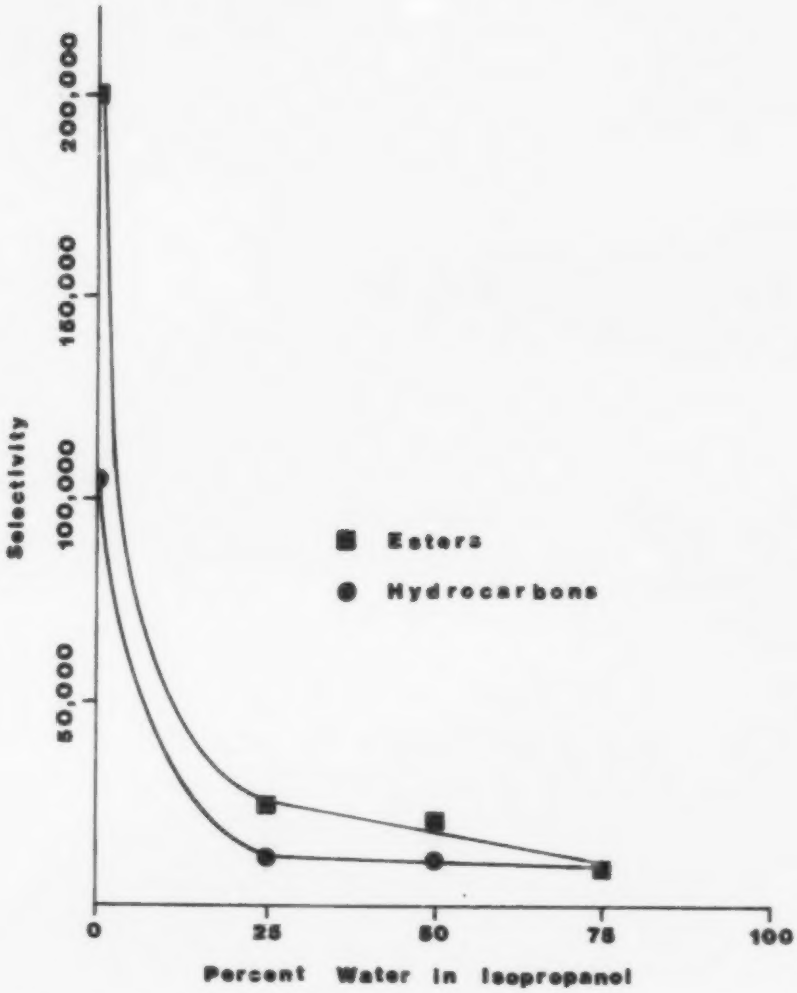


Figure 21. Selectivity to sulfur relative to esters and hydrocarbons versus water content of the conductivity solvent. Conditions: quartz reaction tube; furnace temperature, 950°.

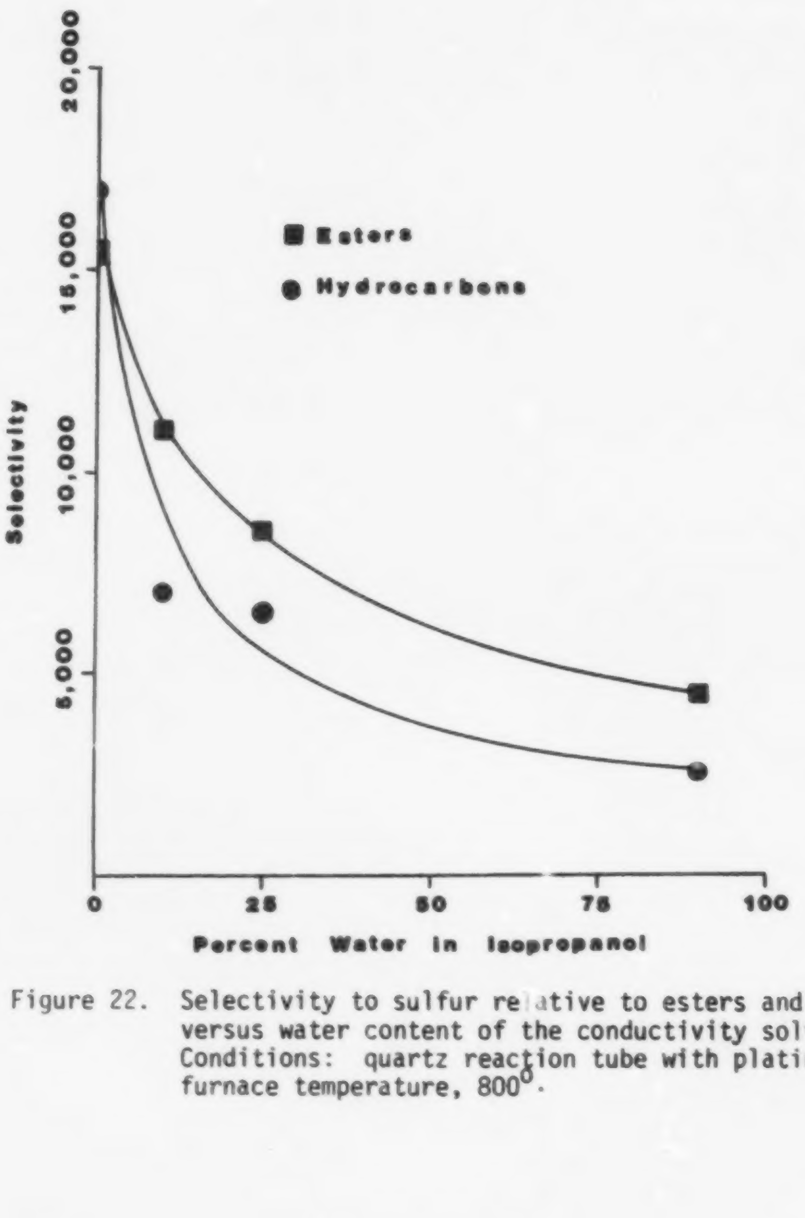


Figure 22. Selectivity to sulfur relative to esters and hydrocarbons versus water content of the conductivity solvent. Conditions: quartz reaction tube with platinum catalyst; furnace temperature, 800°.

Table XXII. Influence of Oxygen Reaction Gas Flow Rate on the Selectivity of the HECD to Sulfur Compounds Using 95% Ethanol as the Conductivity Solvent[a].

| Furnace Temperature | Oxygen Flow Rate<br>2 cc/min | <br>10 cc/min | <br>30 cc/min |
|---|---|---|---|
| 700 | 64,800 | 9,900 | 17,380 |
| 750 | 4,320 | 4,670 | 13,220 |
| 800 | 2,120 | 1,570 | 2,550 |
| 850 | 6,920 | 2,230 | 1,930 |
| 900 | 14,480 | 3,700 | 8,530 |
| 950 | 13,080 | 24,550 | 34,580 |

[a] Reaction tube was empty and 2 mm I.D.

Note: Noise level increased with oxygen flow rate and usable sensitivity was less.

quartz wool than with empty reaction tubes and peak shape is excellent (See Figure 23), the little time that it takes to repack the reaction tube is well spent.

"Reduction of Peak Tailing". Sulfur-containing compounds are not as prone to exhibit peak tailing as chlorine-containing compounds. Nevertheless, peak tailing can occur for small quantities of compound ($\leq$ 10 ng) if the conductivity solvent is not acidic enough or the contact material needs replacing. Use of polar solvent such as methyl alcohol or 75% isopropyl alcohol, periodic replacement of the contact material and application of the techniques developed for the reduction of peak tailing of halogen compounds usually prevent any peak tailing in the analysis of sulfur-containing compounds; and chromatograms similar to those shown in Figures 24-28 should be readily obtained.

Linearity of Detector Response to Sulfur-Containing Compounds. As displayed in Figure 29-31, detector response to sulfur compounds with a polar conductivity solvent is linear over approximately two to four orders of magnitude. The linear dynamic range is very dependent upon the polarity and/or water content of the conductivity solvent. The influence of water content in the conductivity solvent is shown in Figures 32-34. Comparison of these figures reveals that response to diazinon and parathion is linear from $2 \times 10^{-10}$ g to $1 \times 10^{-6}$ g for 10% isopropyl alcohol, but is non-linear at the upper concentration range for 90 and 100% isopropyl alcohol. Linearity at the upper range is better with 75% isopropyl alcohol (Figure 29), but is not as good as with 10% isopropyl alcohol.

Although water is required for the formation of $H_2SO_3$ and $H_2SO_4$ from $SO_2$ and $SO_3$, one microgram of parathion yields only approximately $2 \times 10^{-7}$ g to $3 \times 10^{-7}$ g of $SO_2$ and $SO_3$, which under the conditions of operation requires

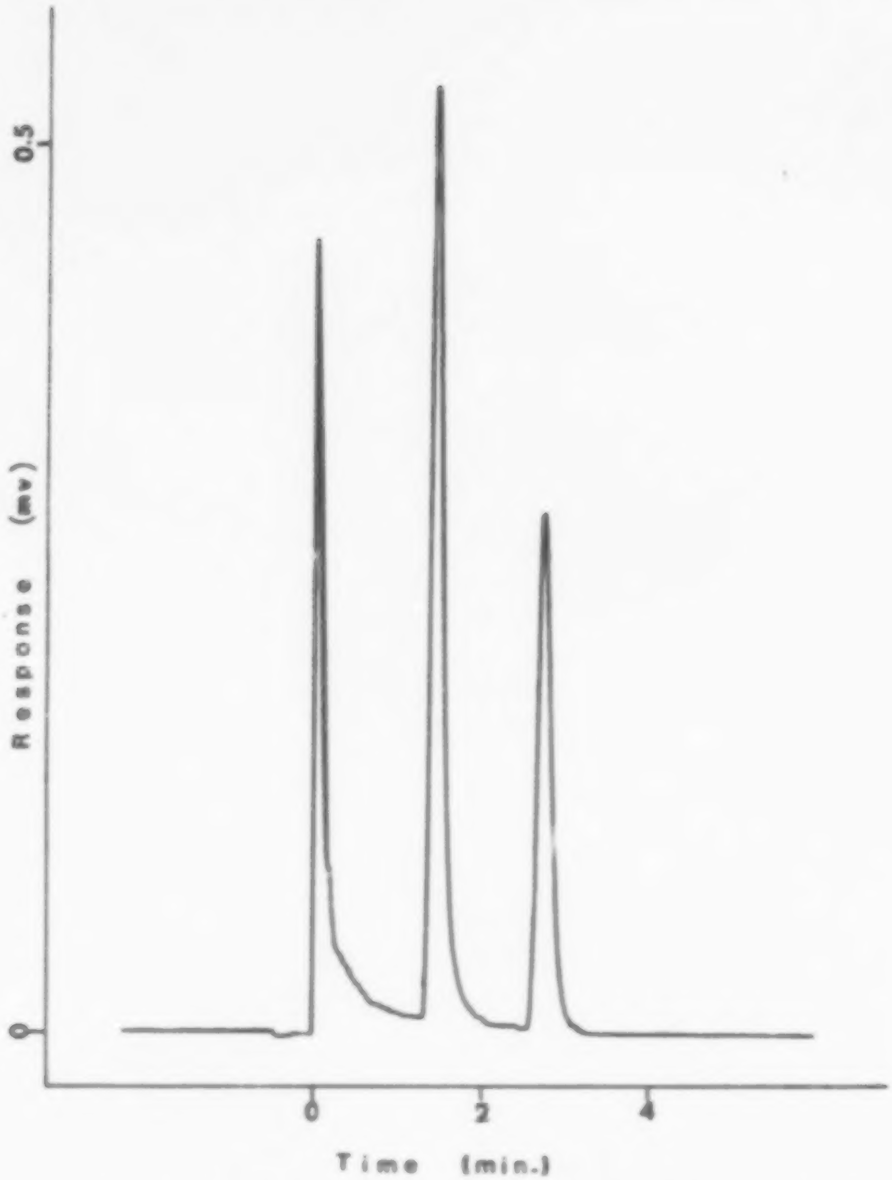


Figure 23. Chromatogram of diazinon and parathion. Conditions: furnace temperature, 700°, reaction tube, 1-mm. i.d. with quartz wool contact material; $O_2$ reaction gas, 4 cc/min; conductivity solvent, methyl alcohol; sample size, 5 ng.

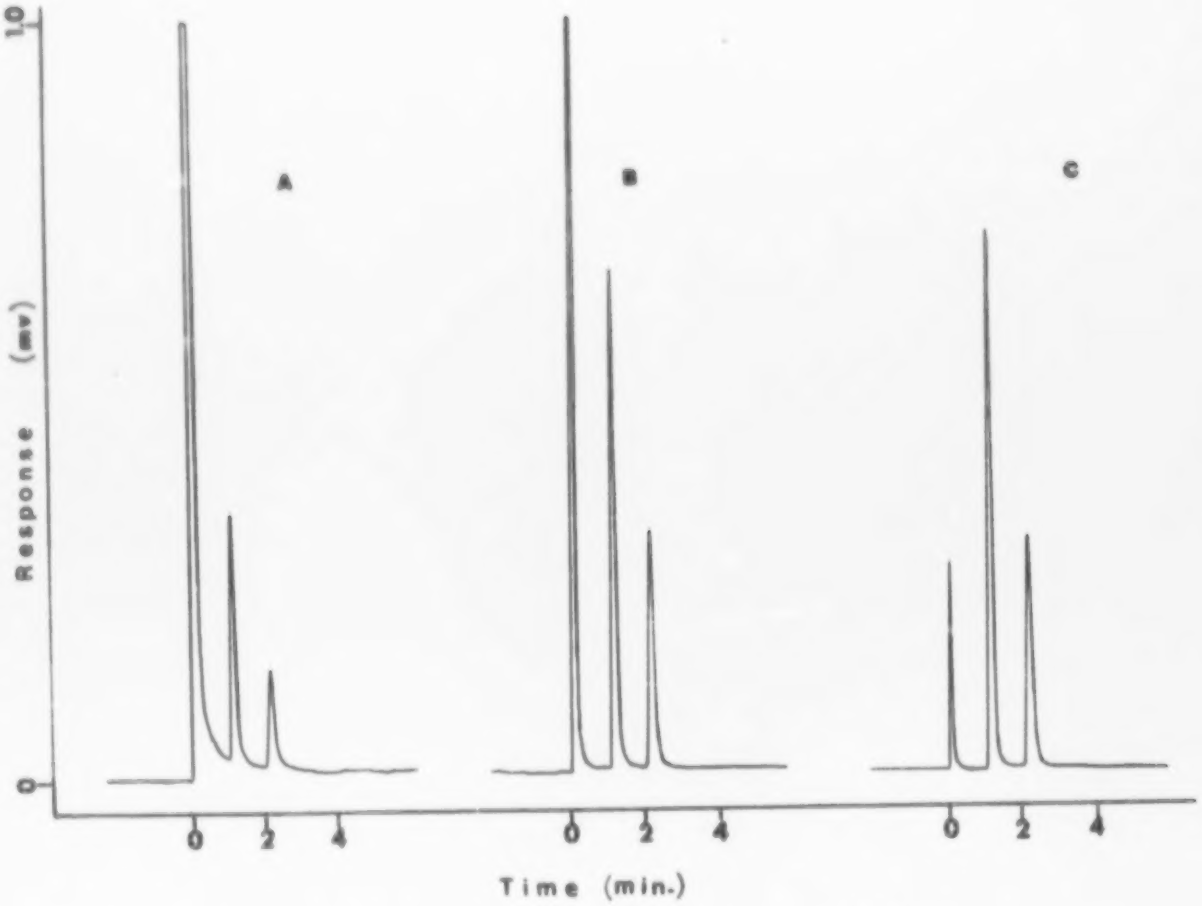


Figure 24. Chromatograms of diazinon and parathion with a platinum catalyst. Conditions; furnace temperature, 725°; $O_2$ reaction gas, 4 cc/min; conductivity solvent, 10% isopropyl alcohol; sample size, A = 1 ng, B = 10 ng, C = 100 ng; attenuation, A = 10 X 0.4, B = 10 X 3.2, C = 100 X 3.2.

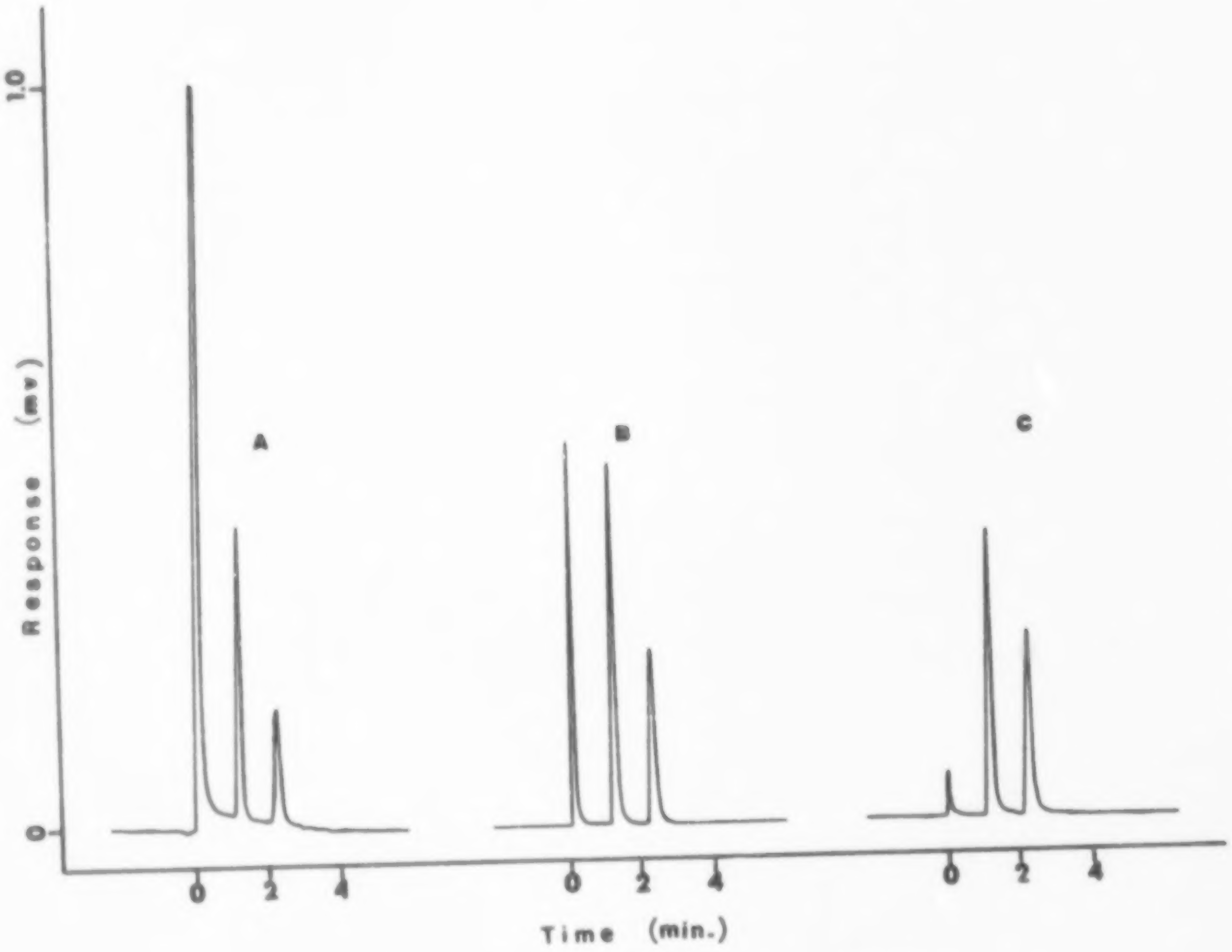


Figure 25. Chromatograms of diazinon and parathion with a platinum catalyst. Conditions: furnace temperature, 725°; $O_2$ reaction gas, 4 cc/min; conductivity solvent, 75% isopropyl alcohol; sample size, A = 1 ng, B = 10 ng, C = 100 ng; attenuation, A = 1 X 0.4 , B = 10 X 0.4, C = 100 x 0.4.

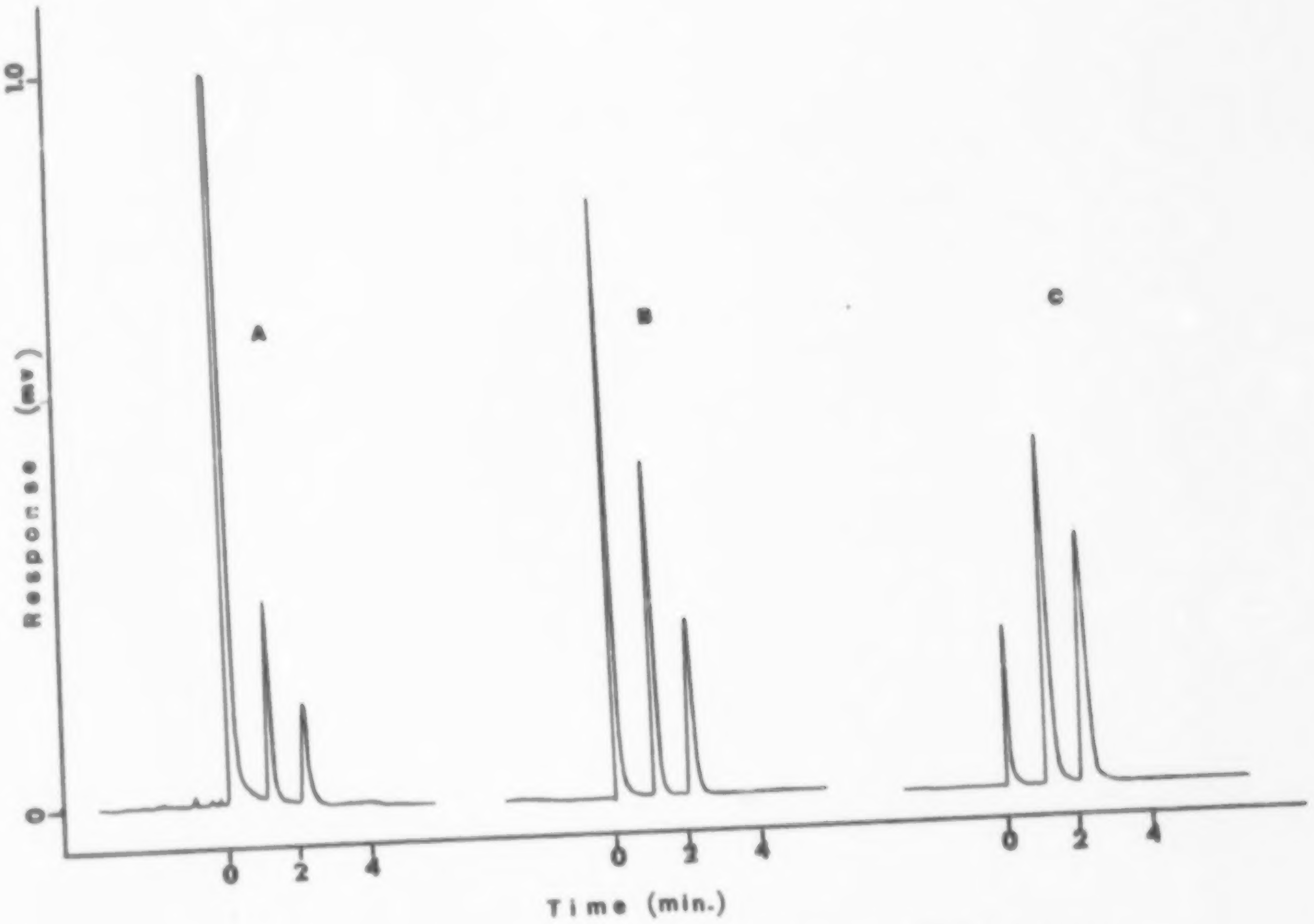


Figure 26. Chromatograms of diazinon and parathion with a platinum catalyst. Conditions: furnace temperature, 800°, $O_2$ reaction gas, 4 cc/min; conductivity solvent, 100% isopropyl alcohol; sample size, A = 2 ng, B = 10 ng, C = 100 ng; attenuation, A = 1 X 0.4, B = 1 X 1.6, C = 10 X 0.8.

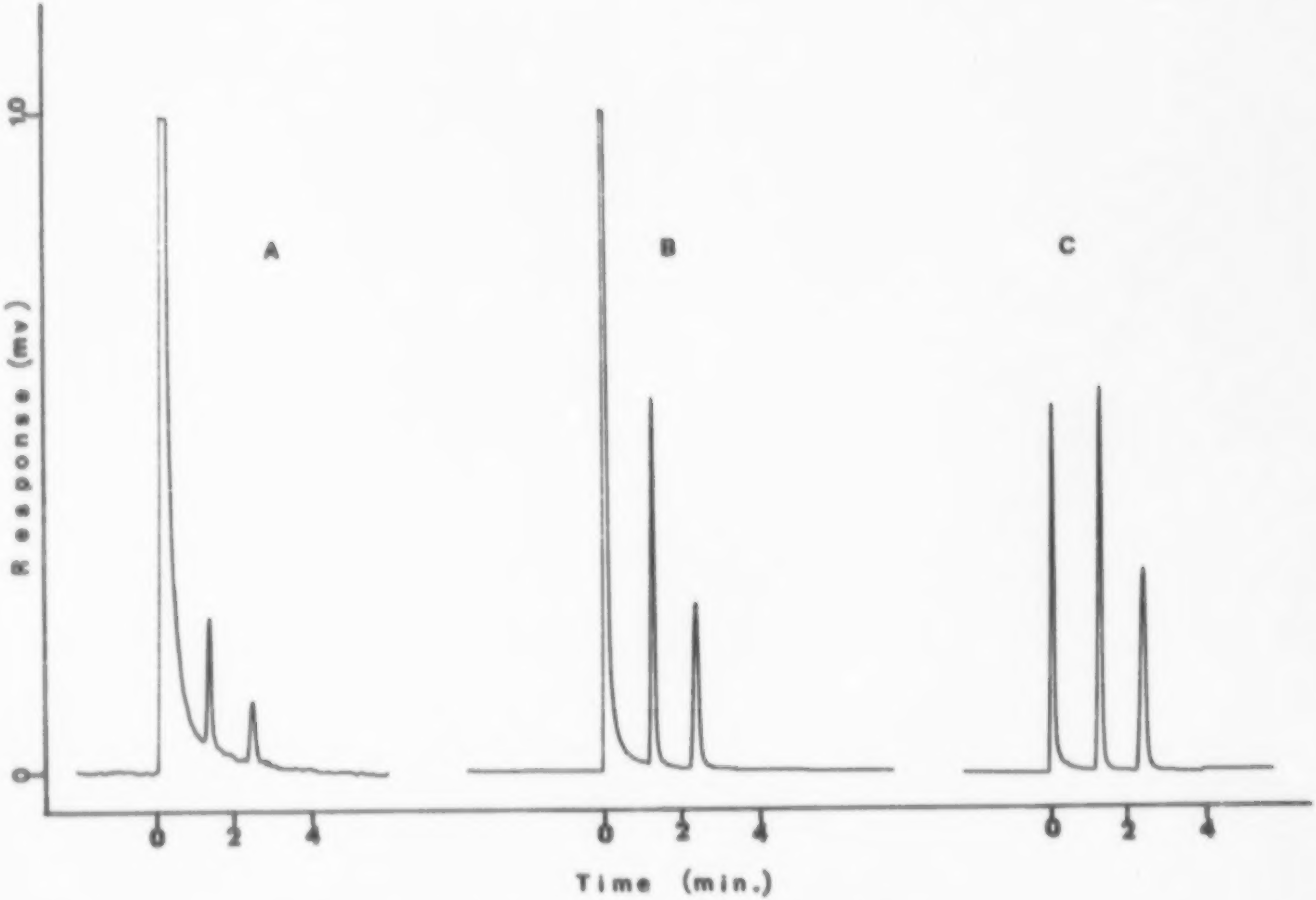


Figure 27. Chromatograms of diazinon and parathion with an empty quartz reaction tube. Conditions: furnace temperature, 900°; $O_2$ reaction gas, 5 cc/min; conductivity solvent, 50% isopropyl alcohol; sample size, A = 1 ng, B = 10 ng, C = 100 ng; attenuation, A = 10 X 0.4, B = 10 X 1.6, C = 10 X 12.8.

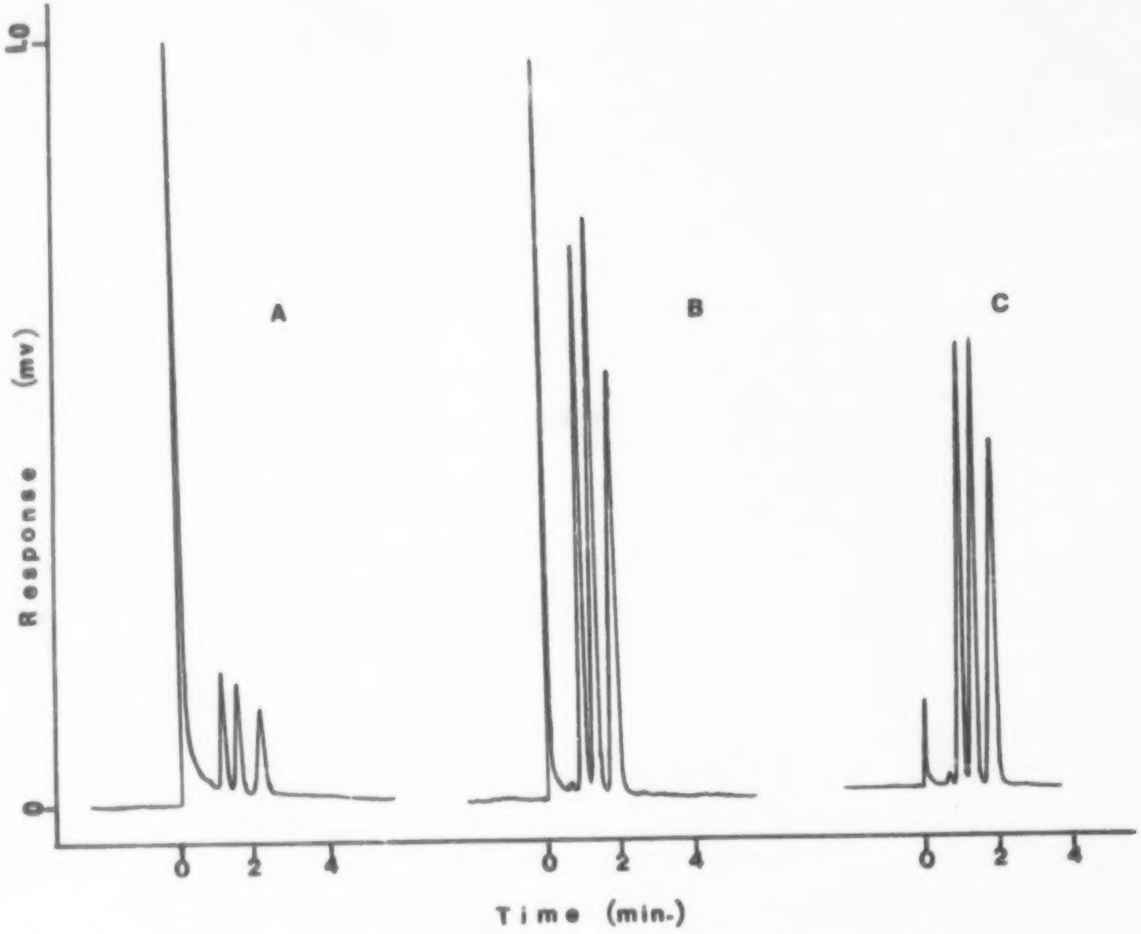


Figure 28. Chromatograms of diazinon, methyl parathion and parathion with an empty quartz reaction tube. Conditions: furnace temperature, 850$^0$; air reaction gas, 20 cc/min; conductivity solvent, methyl alcohol; sample size, A = 2.5 ng, B = 25 ng, C = 250 ng; attenuation, A = 1 X 1.6, B = 10 X 1.6, C = 100 X 1.6.

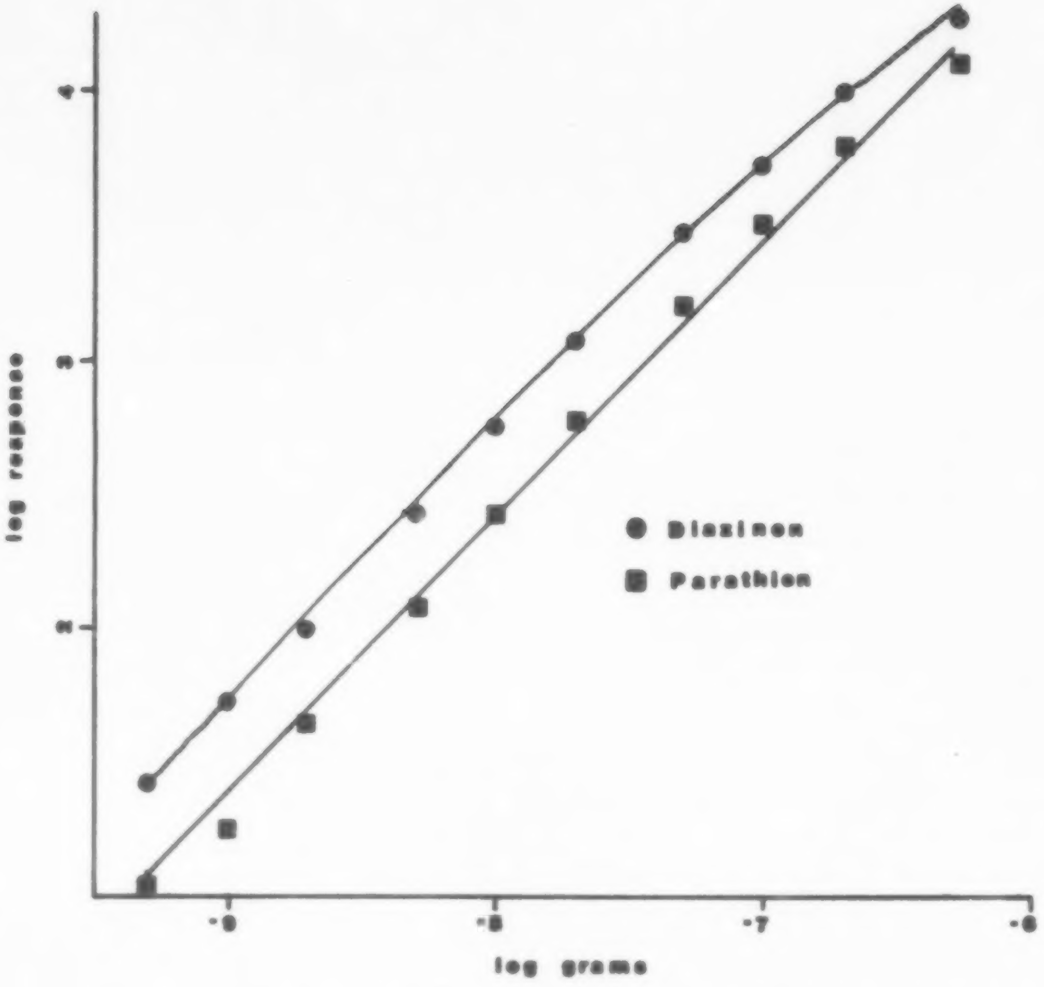


Figure 29. Linearity of response to diazinon and parathion. Conditions: reaction tube, 2-mm. i.d.; furnace temperature, 900°; $O_2$ reaction gas, 4 cc/min; conductivity solvent, 75% isopropyl alcohol.

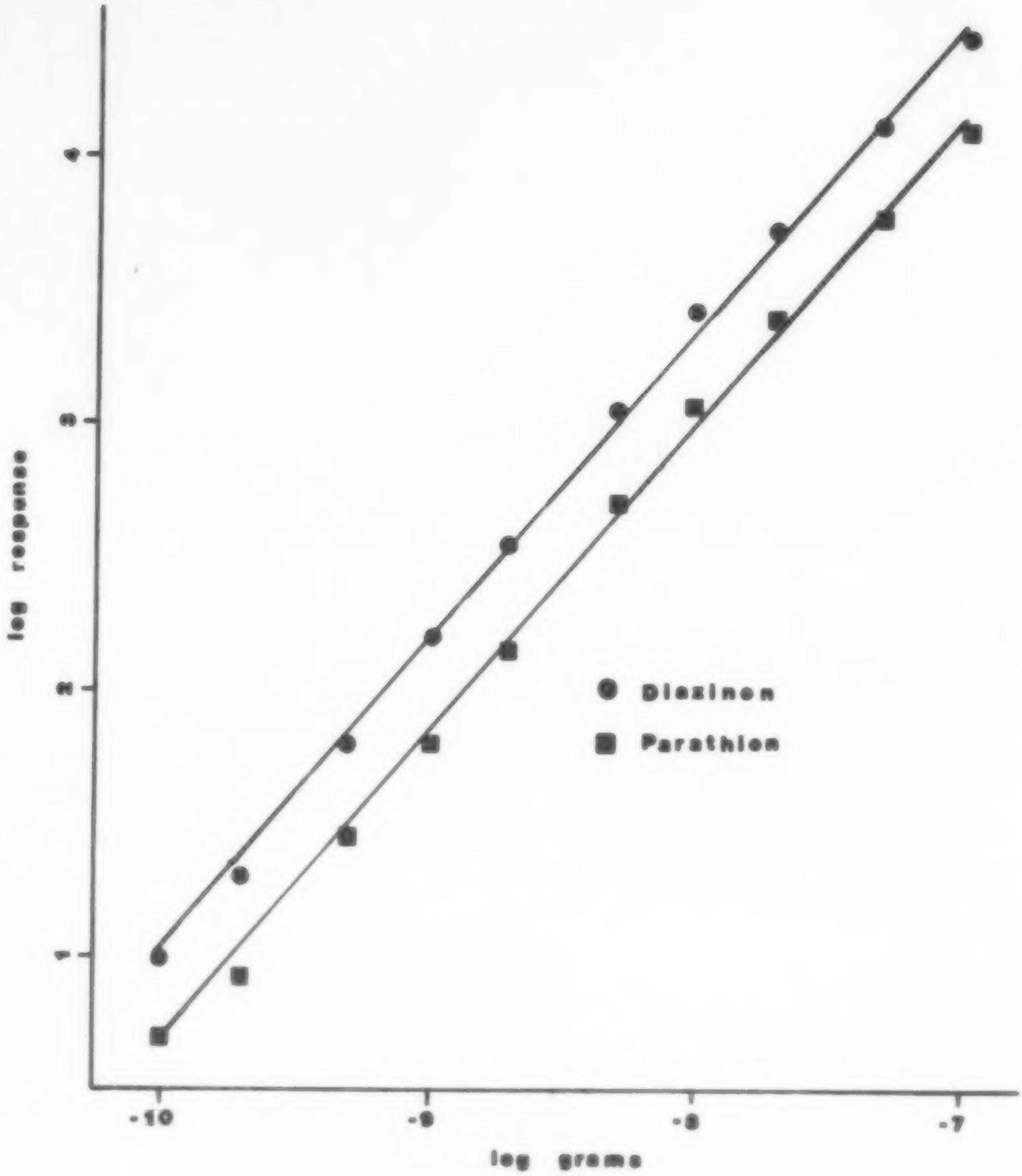


Figure 30. Linearity of response to diazinon and parathion with a platinum catalyst. Conditons: furnace temperature, 725°, $O_2$ reaction gas, 4 cc/min; conductivity solvent, 10% isopropyl alcohol.

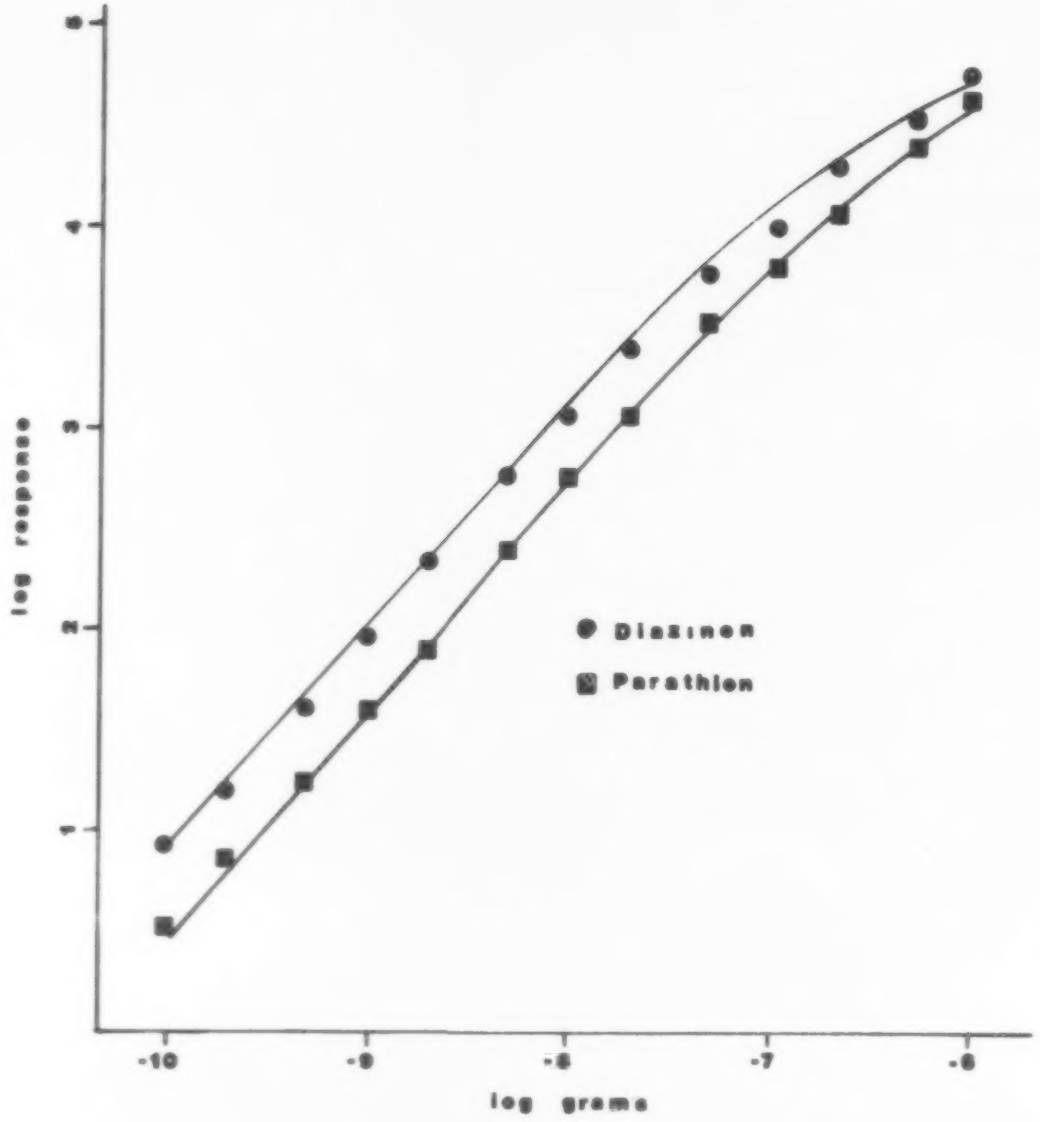


Figure 31. Linearity of response to diazinon and parathion with a platinum catalyst. Conditions: furnace temperature, $725^0$; $O_2$ reaction gas, 4 cc/min; conductivity solvent, 75% isopropyl alcohol.

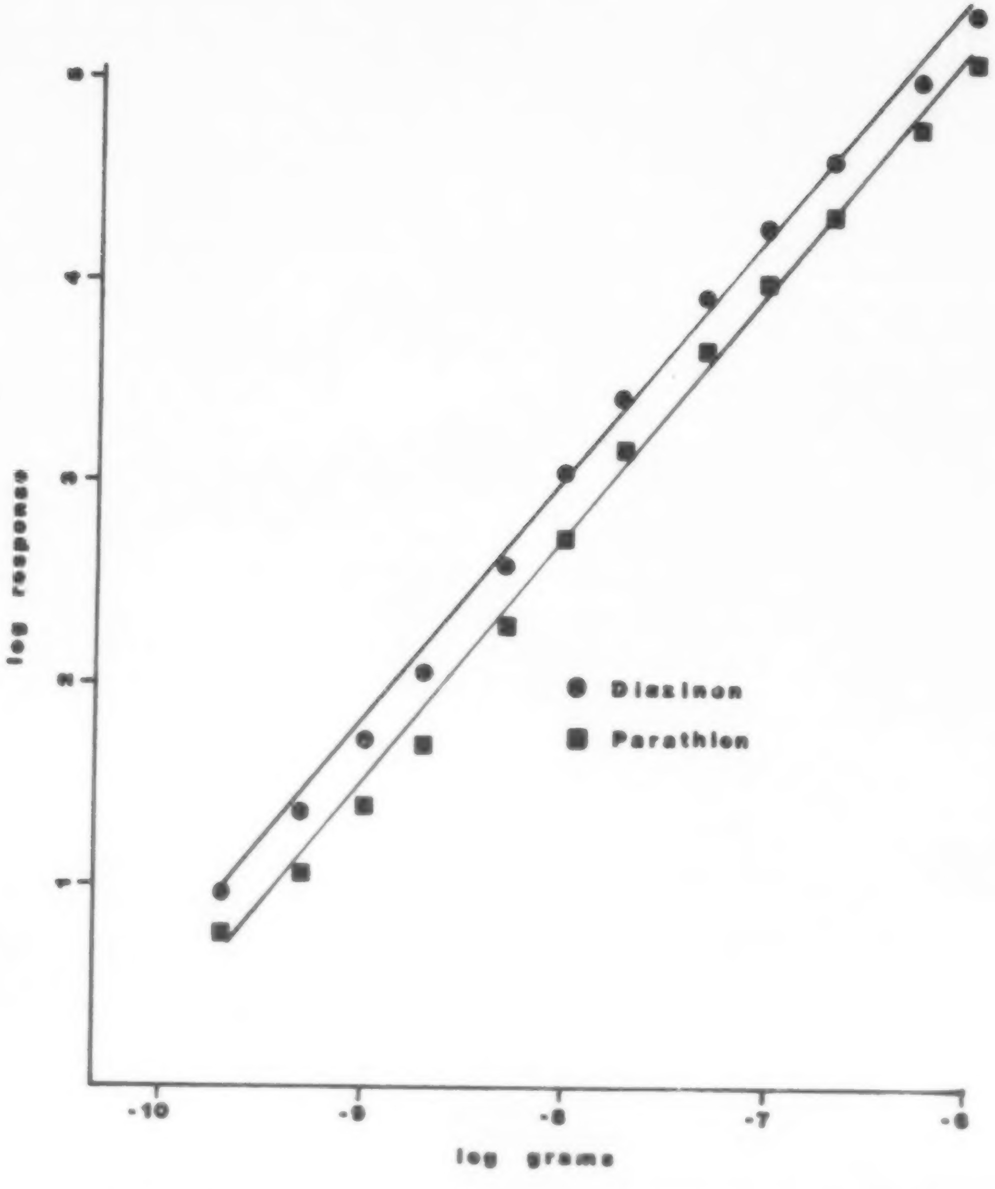


Figure 32. Linearity of response to diazinon and parathion with a platinum catalyst. Conditions: furnace temperature, 800°; $O_2$ reaction gas, 4 cc/min; conductivity solvent, 10% isopropyl alcohol.

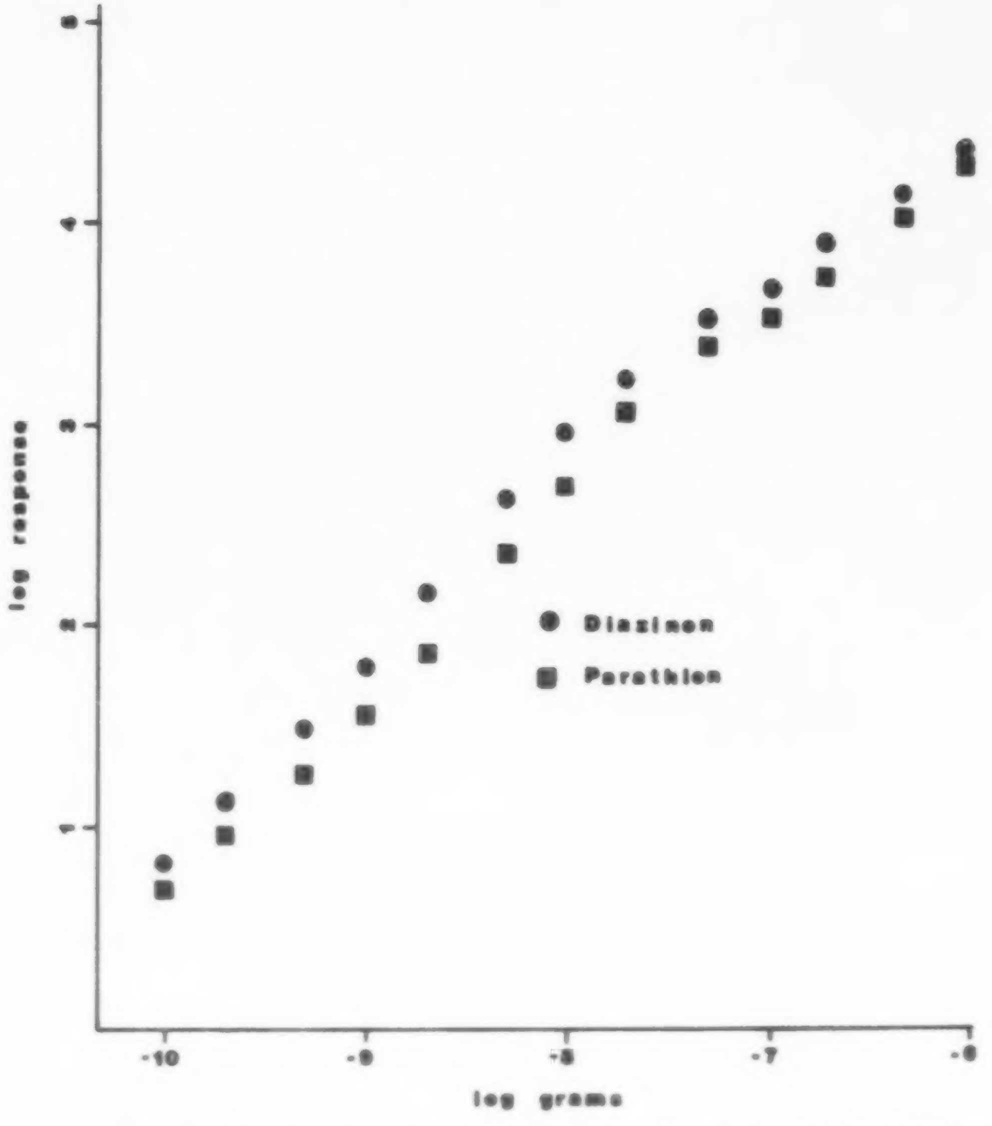


Figure 33. Linearity of response to diazinon and parathion with a platinum catalyst. Conditions: furnace temperature, 800$^0$, $O_2$ reaction gas, 4 cc/min; conductivity solvent, 90% isopropyl alcohol.

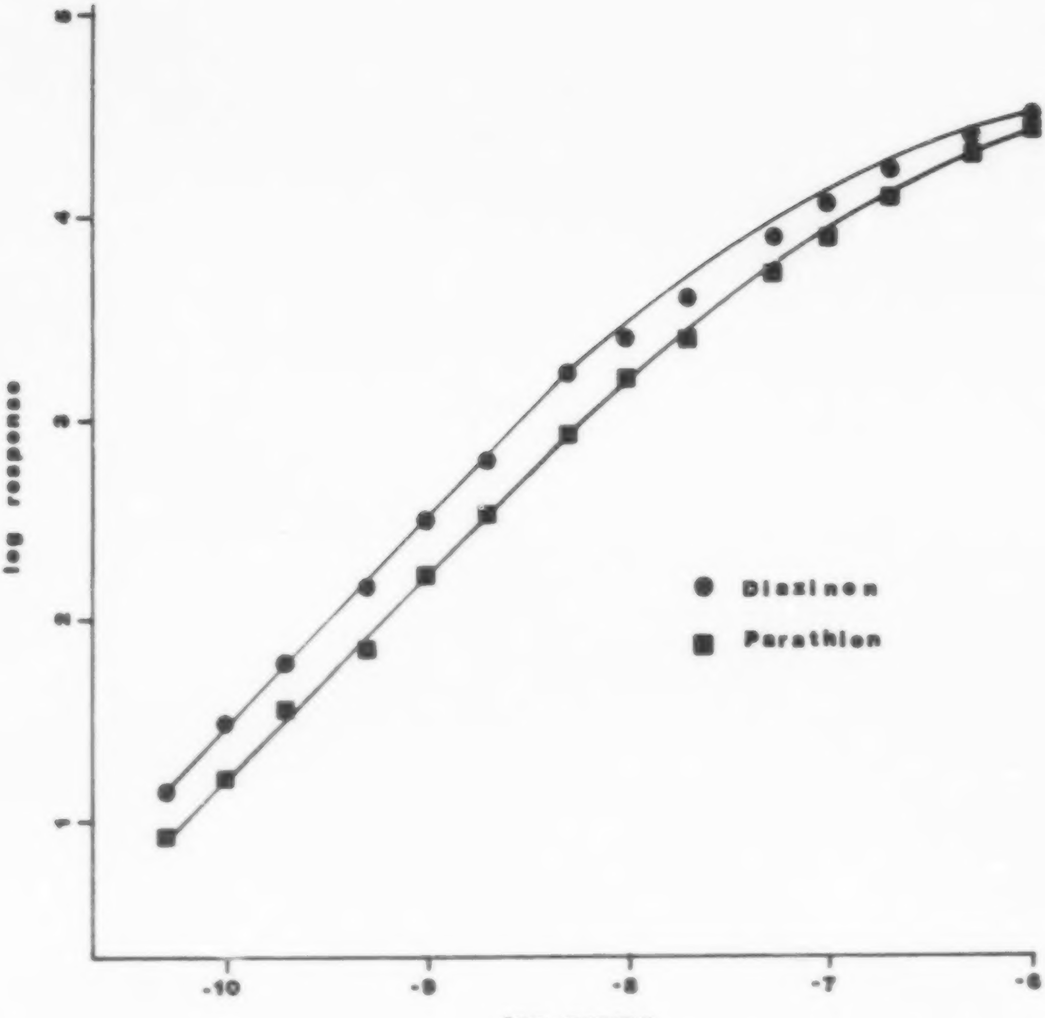


Figure 34. Linearity of response to diazinon and parathion with a platinum catalyst. Conditions: furnace temperature, 800°; $O_2$ reaction gas, 4 cc/min; conductivity solvent, 100% isopropyl alcohol.

approximately 1 X $10^{-6}$ g/ml of water. Thus, even "100%" isopropyl alcohol should contain sufficient water for the conversion of $SO_2$ and $SO_3$ to their respective acids. The improvement in linearity at the upper concentration range with water content of the conductivity solvent may therefore be a function of solvent polarity, which is supported by the fairly good linearity exhibited with methyl alcohol (See Figure 35).

Detector linearity at the upper concentration range is not significantly influenced by the inside diameter of the reaction tube (Figure 29 and 36) or the presence of quartz wool contact material (37). However, linearity at the lower end of the concentration range is very sensitive to the condition of the reaction tube and contact material. In some instances, poor response due to a contaminated reaction tube can be improved by heating the tube overnight at 950° with approximately 50 cc/min. of oxygen reaction gas.

Influence of Conductivity Cell Geometry on Detector Specificity to Sulfur-Containing Compounds. Coulson[2] suggested that the selectivity to sulfur compounds relative to hydrocarbons observed with the Coulson electrolytic conductivity detector may be due to the very short gas-liquid contact time; and since $CO_2$ is slower to dissolve in water than $SO_2$ and $SO_3$, selectivity to sulfur compounds should be observed. In an attempt to enhance detector specificity to sulfur compounds, a conductivity cell that was designed to minimize gas-liquid contact time and solvent surface area was compared to the conventional cell of the Model 310 Hall Electrolytic Conductivity Detector.

Details of design of the conventional cell and the alternate embodiment are shown in Figures 38 and 39, respectively. In the conventional cell, the conductivity solvent and the gaseous reaction products are combined in a small Teflon tee (the gas-liquid contactor). Since the solvent has little affinity for the Teflon surface and the i.d. of the tee is small, the gas and liquid

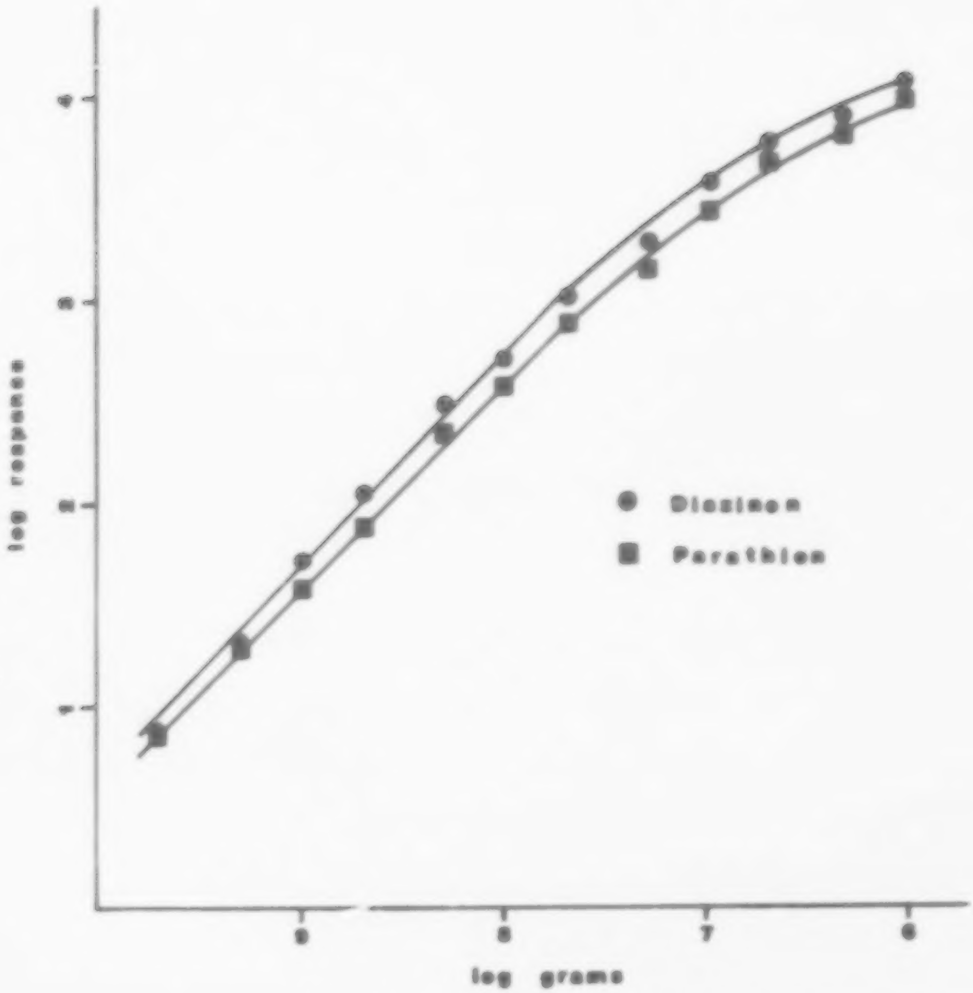


Figure 35. Linearity of response to diazinon and parathion with a quartz wool contact material. Conditions: furnace temperature, 850°; air reaction gas, 12 cc/min; conductivity solvent, methyl alcohol.

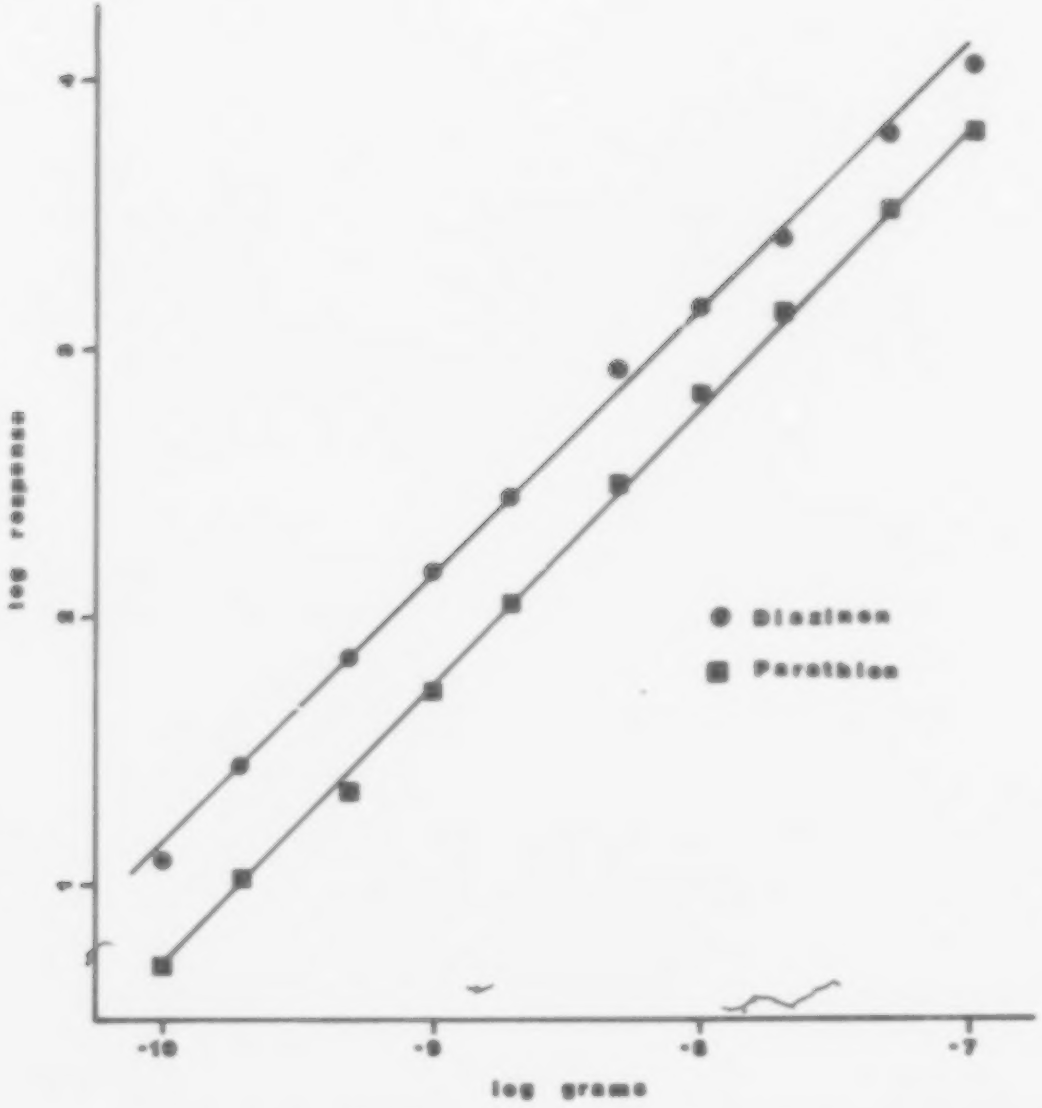


Figure 36. Linearity of response to diazinon and parathion. Conditions: reaction tube, 1 mm. i.d. quartz; furnace temperature, 900°; $O_2$ reaction gas, 4 cc/min; conductivity solvent, 75% isopropyl alcohol.

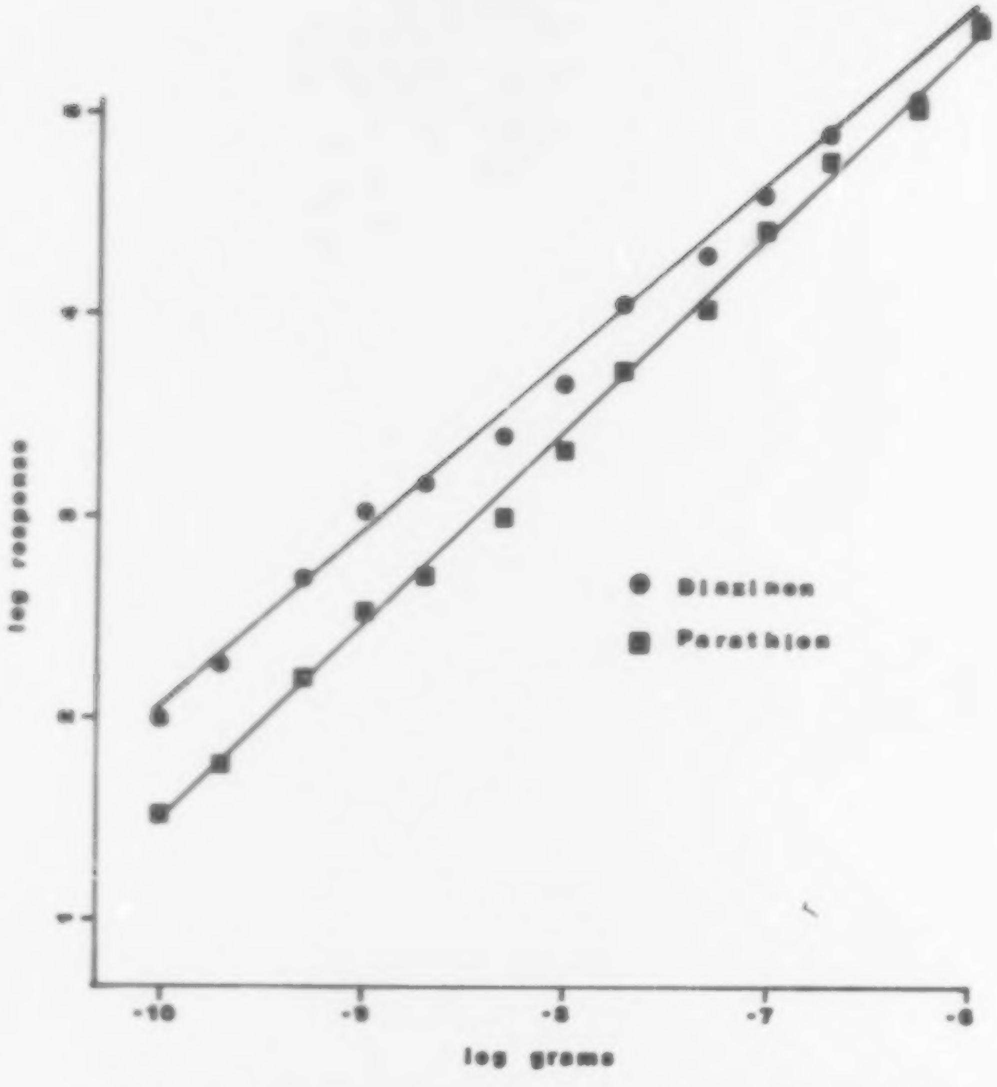


Figure 37. Linearity of response to diazinon and parathion. Conditions: furnace temperature; 625°; $O_2$ reaction gas, 4 cc/min; conductivity solvent, 25% isopropyl alcohol.

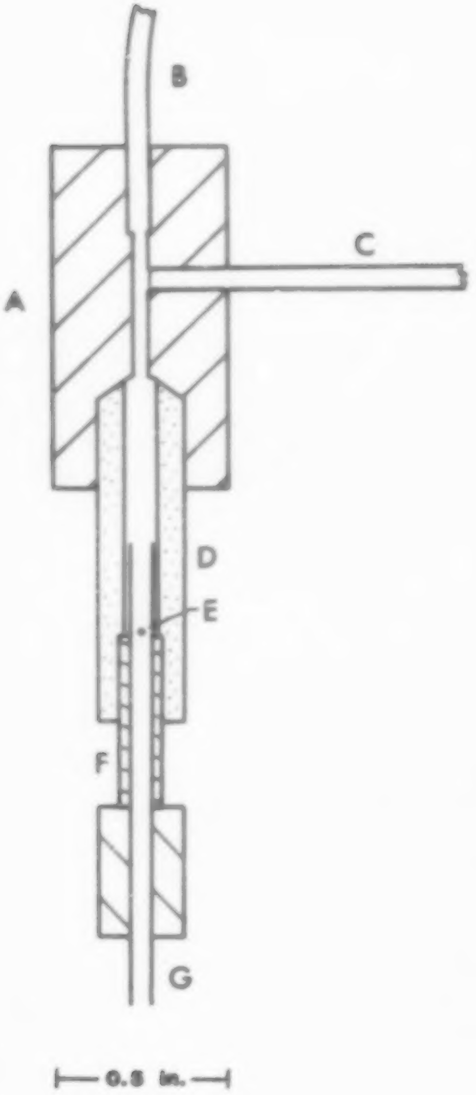


Figure 38. Microelectrolytic conductivity detector cell assembly: A, gas-liquid contactor; B, Teflon solvent delivery tube; C, Teflon reaction products delivery tube; D, stainless steel detector block; E, solvent vent (0.02 in); F, Teflon insulator sleeve; G, gas-liquid exit tube and center electrode.

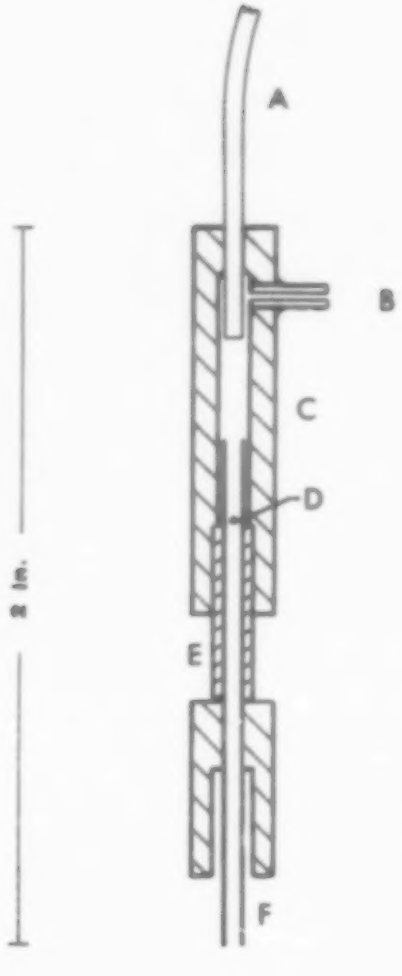


Figure 39. Alternate microelectrolytic conductivity cell assembly: A, gas entrance tube; B, solvent entrance; C, stainless steel detector block; D, solvent vent (0.02 in); E, Teflon insulator sleeve; F, gas-liquid exit tube and center electrode.

phases are well mixed. The heterogeneous gas-liquid mixture thus formed separates into two smooth flowing gas and liquid phases upon contact with the stainless steel surface of the outer electrode (Figure 38, D). The liquid phase flows down the wall as a sheath with the gas phase as the core. In so doing, the liquid phase passes between the inside wall of the detector block (outer electrode) and the outside wall of the inner gas exit tube (Figure 38, G). The solvent is finally vented via the solvent exit hole (Figure 38, E) in the center electrode. In contrast, a heterogeneous gas-liquid mixture is not formed in the conductivity cell design illustrated in Figure 39. In this design, the solvent enters from the side of the cell assembly (Figure 39, B) and proceeds around the Teflon gas entrance tube (Figure 39, A) and then flows down the inside wall of the outer electrode (Figure 39, C). From this point on the liquid and gas phases follow the same paths as described for the other design. Since the gas and liquid phases are not mixed, extraction of soluble gases occurs only at the gas-liquid interface. The gas-liquid contact time and the solvent area exposed to the gas phase can be altered by the distance that the Teflon gas entrance tube is inserted into the cell.

The two cell designs were evaluated using a platinum catalyst and 25% isopropyl alcohol. Detector responses to diazinon (5 ng), parathion (5 ng) and a normal alkane mixture (2 µg each of $C_{16}$, $C_{18}$, $C_{20}$, and $C_{21}$) were determined using the conventional cell and the alternate embodiment with the Teflon gas entrance tube inserted to various depths. Inserting the gas entrance tube further into the cell decreased response to hydrocarbons. However, it also decreased response to the sulfur compounds by the same amount, and no noticeable increase in selectivity was achieved by varying the solvent surface area and the gas-liquid contact time. The two cell designs exhibited essentially equivalent selectivities.

An additional study was conducted to determine if the response to hydrocarbons could be enhanced by greatly increasing the gas-liquid contact time. In this study, the gas and liquid phases were mixed in a Teflon tee and then passed through a 0.03-in. i.d. X 13-in. Teflon tube prior to the conductivity cell. Again, however, response exhibited no significant change.

It can be concluded from these studies that gas-liquid contact time does not appreciably affect selectivity of the Hall Electrolytic Conductivity Detector. Selectivity to sulfur compounds relative to hydrocarbons and esters must therefore merely be a function of the relative quantities of $SO_2 + SO_3$ and $CO_2$, and their relative degree of ionization.

Evaluation of Nickel Tubing for the Detection of Sulfur-Containing Compounds in the Catalytic Oxidative Mode. Considerable variability is encountered in the detection of sulfur compounds with an empty quartz tube or a quartz tube containing a contact material (or catalyst). This variability is usually due to the condition of the reaction tube changing with time. A reaction tube packed with a contact material or catalyst is particularly susceptible to "poisoning" since the flow of gas may be restricted in certain parts of the tube due to uneven packing. The area of the tube where the flow stagnates is prone to carbonization and accumulation of other contaminants from column and sample bleed.

A reaction tube that has an open and unrestricted path for gas flow, moderate and constant surface reactivity, and low adsorption of the reaction products should improve detector performance. Nickel tubing has these properties and was therefore evaluated for the detection of sulfur-containing pesticides. Nickel tubing of the same length and internal dimensions as used for the analysis of chlorine-containing compounds was used. Detector sensitivity and specificity were determined using the same samples as employed in the quartz reaction tube studies.

The nickel reaction tubes require several days for equilibration. Peak shape and sensitivity is usually poor until the tube has been conditioned at furnace operating conditions for at least overnight. After conditioning, however, sensitivity and peak shape are excellent. Chromatograms of a variety of sulfur-containing pesticides are reproduced in Figures 40 and 41.

The need for conditioning is probably due to contamination of the tubing during fabrication. It also probably takes a finite length of time to form a steady-state layer of oxide and to deactivate any adsorptive sites. Heating the outer end of the tube with a torch does not appear to help, and usually increases tailing. Although not investigated in detail, furnace temperature and reaction gas flow rate do not seem to affect conditioning time. Preconditioning the tube by rinsing with acids or bases was not tried, but the tube was rinsed with water and organic solvents to remove any soluble contaminants.

The effects of furnace temperature and reaction gas flow rate on detector response and selectivity to sulfur-containing compounds are presented in Tables XXIII-XXVI. Detector response is reported relative to the peak height at 600$^{0}$ which was assigned a value of 10. Selectivites were calculated from peak heights and reported on a response per gram of sulfur relative to gram of hydrocarbon or ester.

Detector response increases with furnace temperature from 600 to 750$^{0}$ and then decreases with higher temperatures (Table XXIII). However, selectivity relative to hydrocarbons and esters is maximum at 650$^{0}$. Selectivity decreases rapidly with temperature, and is only approximately 150 at 950$^{0}$ (Table XXIV). Though furnace temperature greatly affects detector response, the flow rate of reaction gas does not. Response is maximum between 60 and 100 cc/min. of air, but there is only about a 50% difference between the minimum and maximum values (Table XXV). Flow rate also does not dramatically influence selectivity relative to esters (Table XXVI). The effect of reaction gas flow rate on

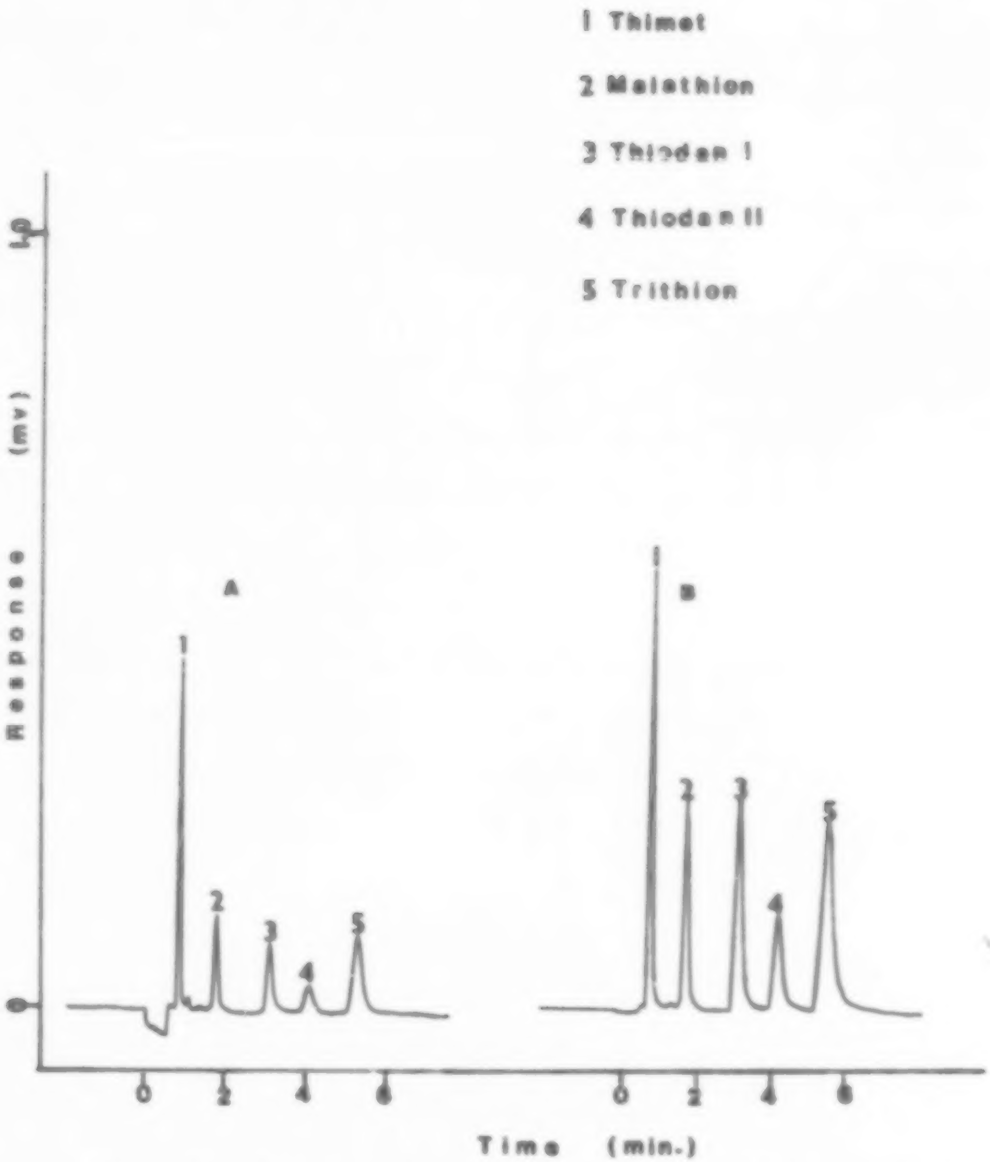


Figure 40. Representative chromatograms of sulfur pesticides with a nickel reaction tube. Conditions: furnace temperature, 850°; air reaction gas, 80 cc/min; conductivity solvent, methyl alcohol; sample size, A = 1 ng, B = 20 ng, attenuation, A = 1 X 0.4, B = 10 X 0.2.

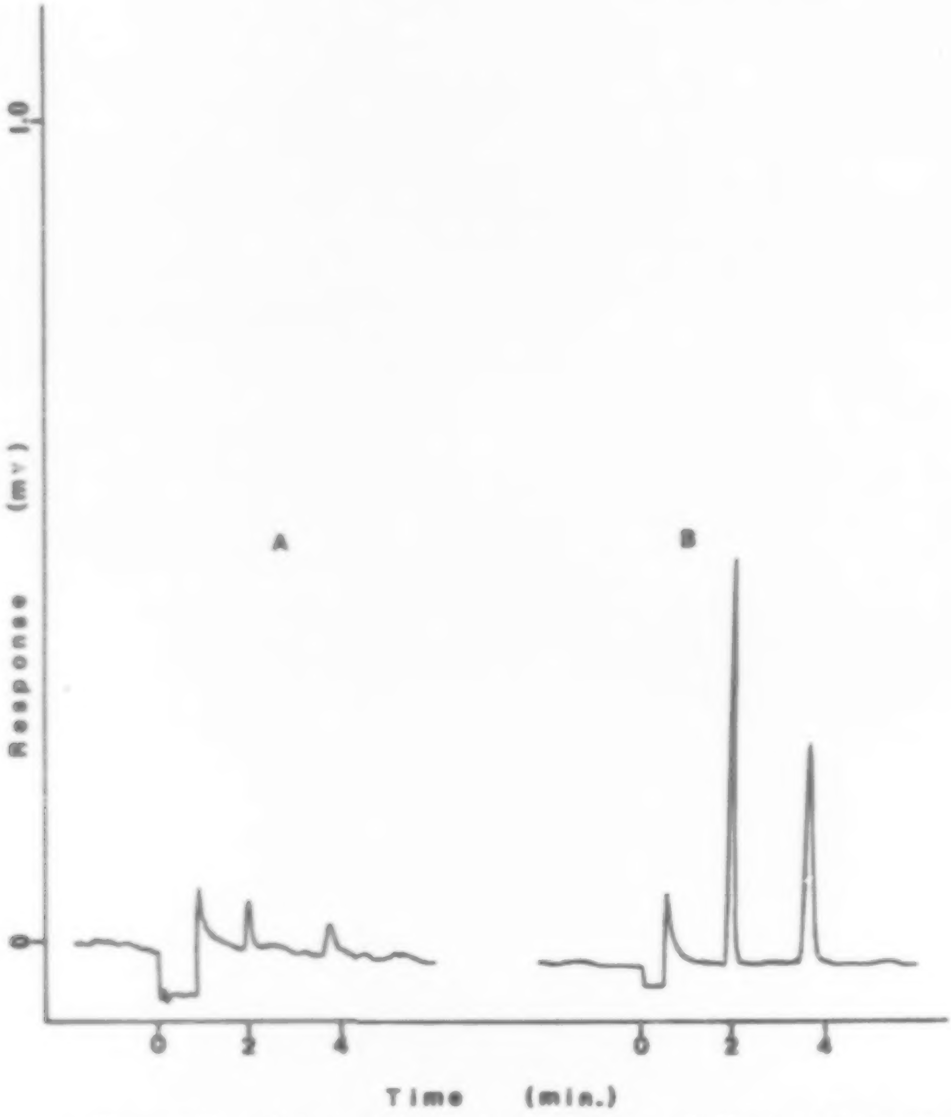


Figure 41. Representative chromatograms of diazinon and parathion with nickel reaction tube. Conditions: furnace temperature, 850°; air reaction gas, 80 cc/min; conductivity solvent, methyl alcohol; sample size, A = 0.5 ng, B = 5 ng; attenuation, A = 1 X 0.2, B = 1 X 0.4.

Table XXIII. Influence of Furnace Temperature on Detector Response to Sulfur-Containing Pesticides in the Catalytic Oxidative Mode Using Nickel Tubing[a,b].

| Compound[c] | Furnace Temperature (°C) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 600 | 650 | 700 | 750 | 800 | 950 | 900 | 950 |
| Diazinon | 10 | 157 | 386 | 557 | 471 | 307 | 147 | 71 |
| Parathion | 10 | 150 | 500 | 725 | 625 | 600 | 300 | 200 |

[a] Detector response reported as relative peak heights with that at 600° assigned a value of 10.

[b] Reaction gas flow rate was 80 cc/min air; conductivity solvent was 25% isopropyl alcohol.

[c] Sample quantity was 2 ng.

Table XXIV. Influence of Furnace Temperature on Detector Selectivity to Sulfur Compounds Relative to Hydrocarbons and Esters in the Catalytic Oxidative Mode Using Nickel Tubing[a].

| Furnace Temperature | Selectivity[b] | |
|---|---|---|
| | Hydrocarbons | Esters |
| 600 | > 11,670 | 1,170 |
| 650 | >183,300 | 4,400 |
| 700 | > 77,140 | 2,060 |
| 750 | 18,570 | 540 |
| 800 | 2,390 | 710 |
| 850 | 990 | 630 |
| 900 | 360 | 350 |
| 950 | 160 | 150 |

[a] Reaction gas flow rate was 80 cc/min air; conductivity solvent was 25% isopropyl alcohol

[b] Selectivity relative to hydrocarbons was calculated from peak heights for diazinon relative to $n$-$C_{12}$, and relative to esters using ethyl dodecanoate. They are based on the response per gram of element detected.

Table XXV. Influence of Reaction Gas Flow Rate on Detector Response to Sulfur-Containing Pesticides.[a,b]

| Compound[c] | Flow Rate (cc/min) | | | | | |
|---|---|---|---|---|---|---|
| | 30 | 60 | 80 | 100 | 150 | 200 |
| Diazinon | 10 | 16 | 12 | 14 | 9 | 9 |
| Parathion | 10 | 16 | 11 | 12 | 6 | 7 |

[a] Detector response reported as relative peak heights with that at 30 cc/min. assigned a value of 10.

[b] Furnace temperature was 650°; conductivity solvent was 25% isopropyl alcohol.

[c] Sample quantity was 2 ng.

Table XXVI. Influence of Reaction Gas Flow Rate on Detector Selectivity to Sulfur Compounds Relative to Esters in the Catalytic Oxidative Mode Using Nickel Tubing.[a]

| | Flow Rate (cc/min) | | | | | |
|---|---|---|---|---|---|---|
| | 30 | 60 | 80 | 100 | 150 | 200 |
| Selectivity[b] | 20,420 | 22,780 | 20,770 | 18,750 | 15,000 | 18,000 |

[a] Furnace temperature was 650°; conductivity solvent was 25% isopropyl alcohol.

[b] Selectivity was calculated from peak heights of parathion and ethyl palmitate.

selectivity relative to hydrocarbons was not investigated since no hydrocarbon response was observed at $650^{0}$.

The influence of furnace temperature on detector selectivity was investigated in greater detail using model compounds of such similar structure that response could be attributed to a single element or functional group. Thioanisole was used to determine sulfur response, m-chlorotoluene for chlorine response and methy o-toluate for ester response.

The detector was operated with 100 % methyl alcohol as the conductivity solvent and 80 cc/min. of air as the reaction gas. Methyl alcohol was used as the conductivity solvent to suppress the nitrogen and ester response. Selectivities were calculated on a response per gram of element or functional group ($-CO_2R$) basis using peak areas. The selectivities are reported in Table XXVII.

Since both halogen- and sulfur-containing compounds can be analyzed in the oxidative mode, little selectivity for sulfur relative to chlorine should be expected; and as shown in Table XXVII, there is indeed little selectivity for sulfur. Selectivity to sulfur relative to halogens can be improved by the use of a silver scrubber[3], if needed.

Selectivity to sulfur relative to nitrogen reaches a maximum of 252 at $825^{0}$, whereas selectivity to esters is at a maximum value of 10,308 at $875^{0}$. Although selectivity relative to esters and hydrocarbons (Table XXIV) should be sufficient for most analyses, selectivity relative to nitrogen may be insufficient. Therefore questionable samples should also be analyzed in the reductive mode.

Minimum Detectable Quantity. The minimum detectable quantity of a sulfur-containing compound depends upon its sulfur content and the operating conditions

Table XXVII. Influence of Furnace Temperature on Sulfur Selectivity in the Catalytic Oxidative Mode.[a,b]

| | Element | | |
|---|---|---|---|
| Furnace Temperature ($^{o}$C) | Cl | N | $\mathrm{R{-}O{-}\underset{\vert}{C}{=}O}$ |
| 750 | 24 | 82 | 1,988 |
| 775 | 24 | 138 | 3,011 |
| 800 | 17 | 183 | 4,100 |
| 825 | 21 | 252 | 6,524 |
| 850 | 19 | 239 | 8,967 |
| 875 | 14 | 167 | 10,308 |
| 900 | 6 | 110 | 6,293 |
| 925 | 2 | 75 | 4,042 |
| 950 | 2 | 84 | 4,444 |

[a] Reaction gas flow rate was 80 cc/min of air; conductivity solvent was 100% methyl alcohol.

[b] Selectivities calculated from peak areas using thioanisole (10 ng), _m_-tolunitrile (500 ng), _m_-chlorotoluene (50 ng), and methyl _o_-toluate (10 μg).

used. In general, minimum detectable quantities are lower when a contact material or catalyst is used. Minimum detectable quantities of 50-100 pg can usually be obtained for diazinon and parathion. Minimum detectable quantities for a variety of sulfur-containing pesticides are presented in Tables XXVIII and XXIX. Representative chromatograms of low levels of pesticides are reproduced in Figures 42 and 43.

Table XXVIII. Minimum Detectable Quantities[a] of Diazinon and Parathion.

| Conditions | Compound<br>Diazinon | <br>Parathion |
|---|---|---|
| 10% Isopropyl alcohol<br>ARM-381<br>FT = 725°, $O_2$ = 4 cc<br>Platinum catalyst | 56 pg<br>(1.12)[b] | 91 pg<br>(2.04) |
| 75% Isopropyl alcohol<br>ARM-381<br>FT 725°, $O_2$ = 4 cc<br>Platinum catalyst | 17 pg<br>(1.16) | 50 pg<br>(2.16) |
| 100% Isopropyl alcohol<br>ARM-381<br>FT 800°, $O_2$ = 4 cc<br>Platinum catalyst | 8 pg<br>(1.12) | 13 pg<br>(2.08) |
| 25% Isopropyl alcohol<br>2/3 IRN-150 + 1/3 IRN-77<br>FT 650°, $O_2$ = 4 cc<br>Quartz wool | 29 pg<br>(1.48) | 100 pg<br>(2.88) |
| 100% Methyl alcohol<br>2/3 IRN-150 + 1/3 IRN-77<br>FT 700°, Air = 100 cc<br>Nickel tube | 40 pg<br>(1.12) | 50 pg<br>(2.00) |

[a] Minimum detectable quantities are that 2X noise and short-term drift.

[b] Values in parenthesis are retention times in minutes.

Table XXIX. Minimum Detectable Quantities of Sulfur-Containing Compounds.[a]

| | Compound | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Conditions | Methyl Parathion | Diallate | Thimet | Malathion | Captan | Thiodan I | Thiodan II | Trithion |
| 100% Methyl alcohol<br>1/2 IRN-150 + 1/2 IRN-77<br>FT = 850°, $O_2$ =12 cc<br>Quartz wool | | 125 pg<br>(0.84) | 9 pg<br>(0.72) | 15 pg<br>(1.68) | 83 pg<br>(2.41) | 39 pg<br>(3.08) | 100 pg<br>(4.16) | 26 pg<br>(5.12) |
| 100% Methyl alcohol<br>1/2 IRN-150 + 1/2 IRN-77<br>FT = 850°, Air = 80 cc<br>Nickel tube | 118 pg<br>(1.44) | 68 pg<br>(0.84) | 34 pg<br>(0.76) | 133 pg<br>(1.68) | | 200 pg<br>(3.04) | 400 pg<br>(4.12) | 182 pg<br>(5.32) |

[a] Minimum detectable quantities are that 2X noise and short-term drift.

[b] Values in parenthesis are retention time in minutes.

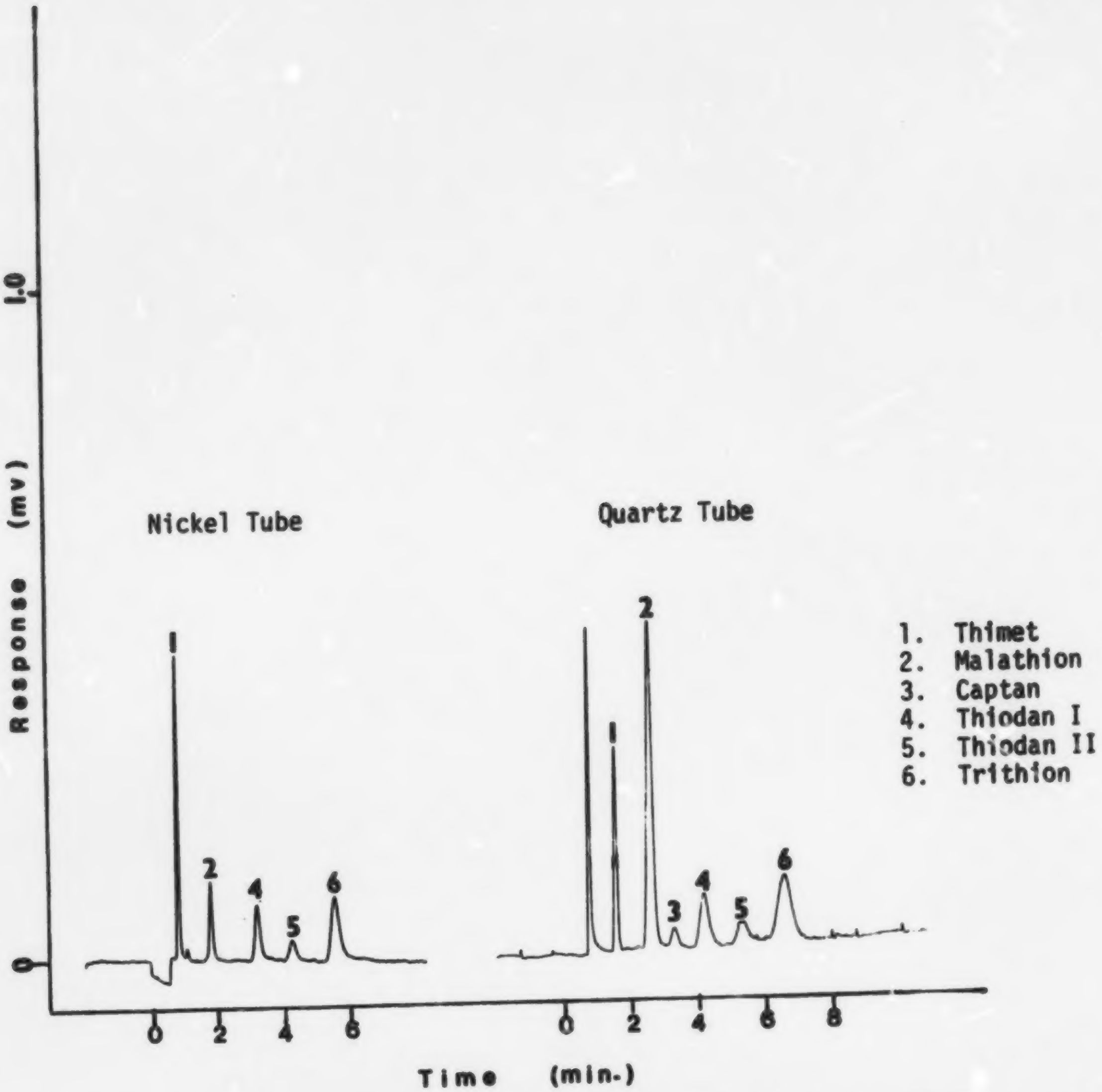


Figure 42. Chromatograms of low levels of sulfur pesticides with nickel and quartz reaction tubes. Conditions: conductivity solvent, methyl alcohol; sample size; nickel tube - 1 ng, quartz tube - 0.5 ng; attenuation, nickel tube - 1 X 0.4, quartz tube - 1 X 1.6.

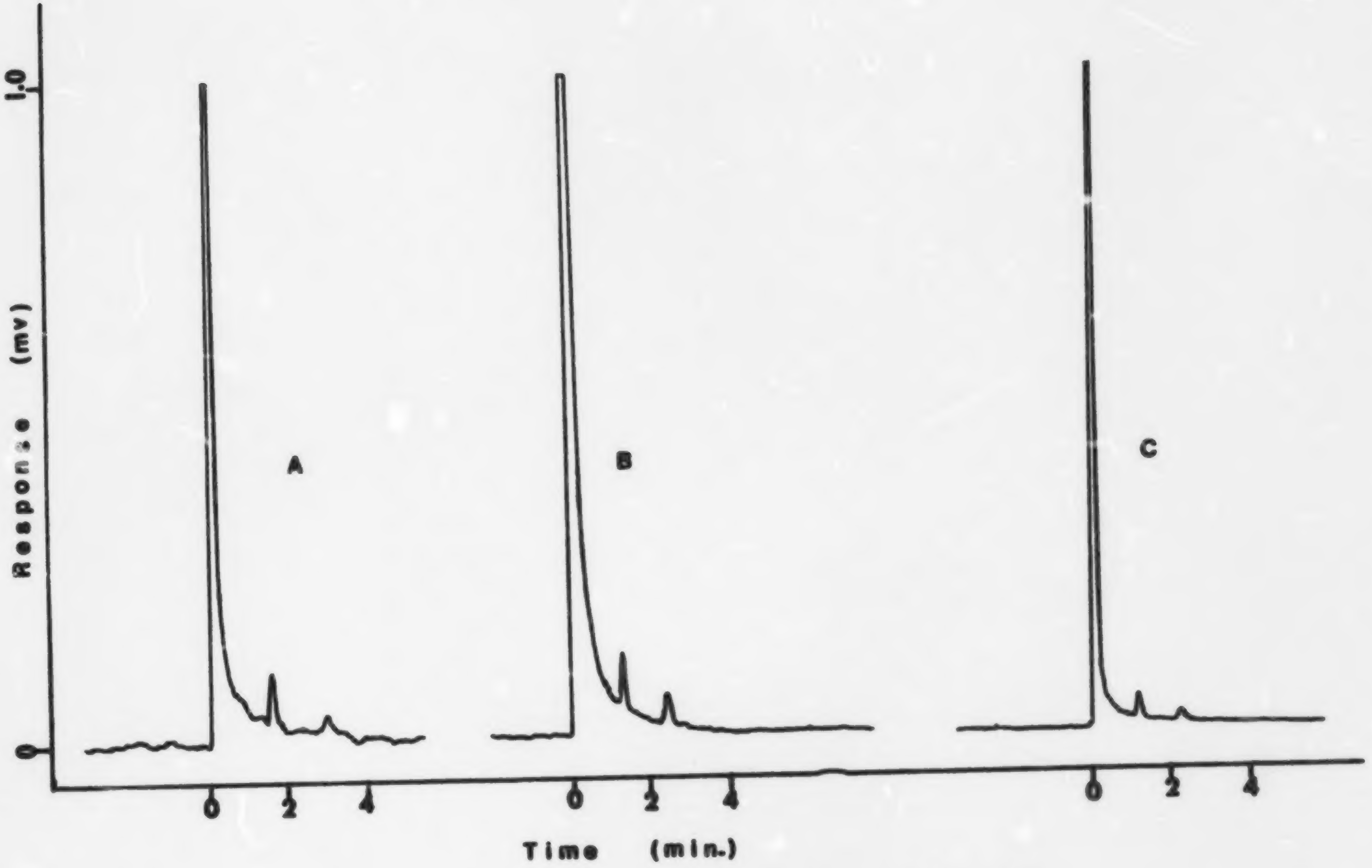


Figure 43. Chromatograms of low levels of diazinon and parathion with different conditions. Conditions (A): 0.1 ng, 25% isopropyl alcohol, $625^0$, quartz wool contact material. Conditions (B): 0.5 ng, 50% isopropyl alcohol, $900^0$, empty quartz tube. Conditions (C): 0.1 ng, 75% isopropyl alcohol, $725^0$; platinum catalyst.

## Detection of Nitrogen-Containing Compounds

Optimization of Detector Operating Conditions. Nitrogen-containing compounds are detected using the catalytic reductive mode. In this mode, $NH_3$, HX, $H_2S$, $H_2O$, $CH_4$ and lower alkanes are produced from organic compounds containing nitrogen, halogen, sulfur and oxygen. Selectivity is acheived by removing HX and $H_2S$ with a strontuim hydroxide abstractor. Water does not give a response since it is already present in large excess in the conductivity solvent. Methane and lower alkanes are not ionized and do not give a response. Thus, selectivity is primarily a function of the capacity and abstracting effeciency of the strontuim hydroxide scrubber.

"Conductivity Solvent and Reaction Systems." Though the conversion of organic nitrogen to $NH_3$ is fairly straight forward, the measurement of trace quantities of $NH_3$ by electrolytic conductivity is not. Ammonia must react with water to form the ammonium and hydroxyl ions which are the charge carriers.

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

However, if the conductivity solvent is acidic, addition of ammonia will result in the formation of an ammonium salt. Since the specific ionic conductance

$$HY + NH_4^+ \ OH^- \rightleftharpoons NH_4^+ + Y^- + H_2O$$

of the ammonium ion is less than that of the proton and most negative ions have a specific ionic conductance less than that of the hydroxyl ion, there will be a decrease in electrolytic conductivity for trace quantities of ammonia.

Thus, the sensitive detection of nitrogen compounds without the formation of negative peaks requires a slightly basic aqueous conductivity solvent that also has a low conductivity. The required basicity and low conductivity can be maintained with an ion exchange resin tube packed with 2/3 Duolite ARA-366 ($OH^-$ form) on the bottom (pump side) and 1/3 IRN-150 on the top (cell side) similar to that previously described by Patchett[4].

Column bleed and impurities in the helium carrier gas may lower the pH of the conductivity solvent and increase detector background. Attempts to use helium as the carrier gas were only partially successful due to the presence of impurities. Consequently, electrolytic hydrogen was used as the carrier and reaction gas. The effect of column bleed, if minor, can be compensated for by the addition of a very small amount (0.01 -0.1 cc/min) of $N_2$ to the reaction gas. Under the conditions of operation, a small percentage of the $N_2$ is converted to $NH_3$, which increases the pH of the conductivity solvent and prevents the formation of negative peaks and loss of sensitivity in the detection of low nanogram quantities of nitrogen compounds.

The addition of $N_2$ to the reaction gas may cause a high and inconsistent background that may take several days to subside. The background, after equilibration, should be approximately 10 to 20% higher than that without $N_2$. The conversion of $N_2$ to $NH_3$ increases substantially from 825 to $875^0$. The most uniform results are obtained at approximately $825^0$.

A variety of solvents and ion exchange resins were investigated for the detection of nitrogen-containing compounds. The solvents included methyl alcohol, acetonitrile, isopropyl alcohol with 0.1% methyl iodide, 1:1 isopropyl alcohol/water, 1:5 dimethylformamide/water, 1:2:20 dimethylformamide/isopropyl alcohol/water, 1:10 acetonitrile/water, 1:10 isopropyl alcohol/water and 1:7 isopropyl alcohol/water. The resins included Amberlite IRN-150, Amberlite IRN-154, Amberlite IRN-78, Duolite ARM-381 and Duolite ARA-366 ($OH^-$ form).

The best performance was obtained with 10-15% isopropyl alcohol in water and a resin tube packed as described above with IRN-150 and ARA-366. The other conductivity solvents resulted in high background and/or poor response. Response with pure water was as good as that obtained with 10% isopropyl alcohol, but the baseline was noisy.

The influence of furnace temperature on detector response to CIPC, atrazine and simazine is shown in Figure 44. Little response is observed below approximately $750^{o}$. Response increases rapidly with temperature up to 800 to $825^{o}$ and continues to increase slightly from 825 to $850^{o}$.

Since the noise level in the presence of $N_2$ also increases with temperature and is excessive at $850^{o}$, the best performance is obtained at approximately $825^{o}$. However, in the absence of $N_2$ (column bleed permitting) a useful increase in sensitivity is obtained by operating at $850^{o}$.

Although response is temperature dependent, considerable changes in the flow rate of the hydrogen reaction gas can be tolerated without adverse effects. The influence of hydrogen reaction gas flow rate on detector sensitivity to CIPC, atrazine and simazine is summarized in Table XXX. It should be noted that the total hydrogen flow rate is 40 cc/min. greater, because 40 cc/min. of hydrogen carrier gas was used. Under these conditions, the addition of 10 to 100 cc/min. of additional hydrogen did not significantly affect detector response. Though there is some variation of response with hydrogen flow rate, the data is inconsistently variable. Repeating the experiment two additional times resulted in the same trend.

The effect of solvent flow rate on detector response is shown in Figure 45. As would be expected, response is inversely proportional to solvent flow

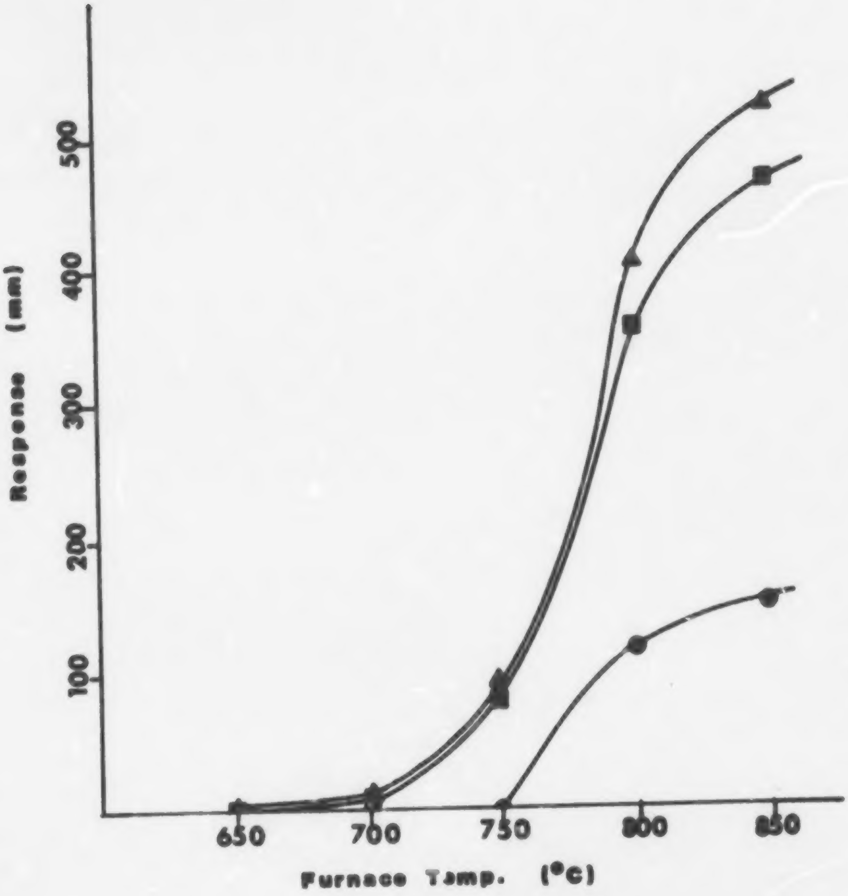


Figure 44. Influence of furnace temperature on response to atrazine (▲), simazine (■) and CIPC (●).

Table XXX. Influence of Hydrogen Reaction Gas Flow Rate on Response to Nitrogen-Containing Compounds[a].

| Flow Rate (cc/min)[c] | Response[b] | | |
|---|---|---|---|
| | CIPC | Atrazine | Simazine |
| 10 | 27 | 89 | 78 |
| 20 | 32 | 109 | 95 |
| 40 | 37 | 121 | 109 |
| 60 | 32 | 108 | 95 |
| 80 | 38 | 131 | 116 |
| 100 | 31 | 108 | 96 |

[a] Furnace temperature was 800°.

[b] Response is peak heights in mm.

[c] Total flow also contained 40 cc/min of $H_2$ carrier.

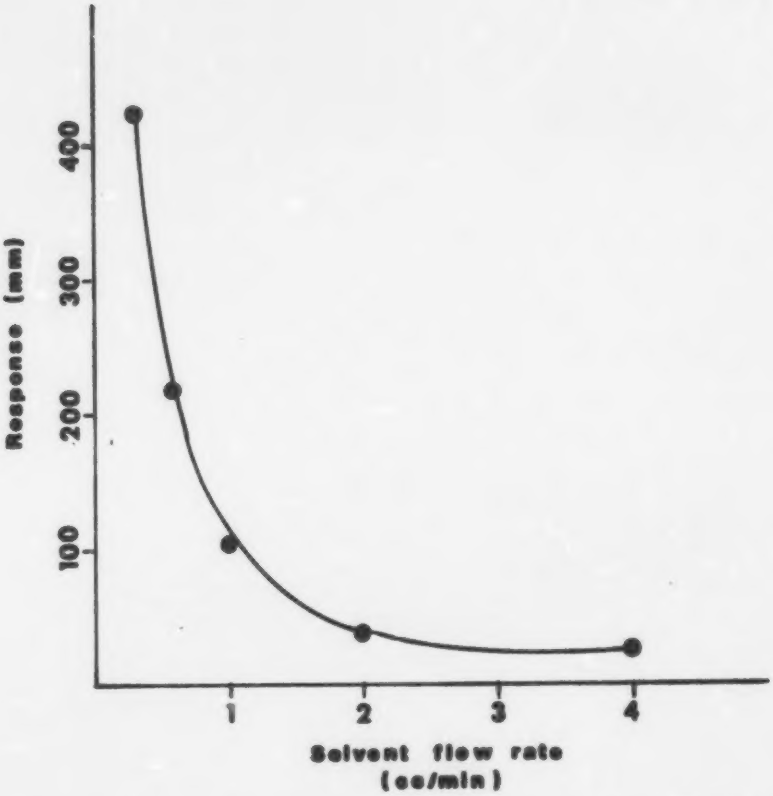


Figure 45. Influence of conductivity solvent flow rate on detector response to atrazine.

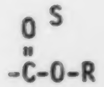
rate. The change in response is a little larger than the calculated value. However, there is some evaporation of the solvent in the cell, and a little larger response with a given decrease in flow rate would therefore be expected.

Although the cell requires a flow rate 0.3 cc/min. to prevent peak broadening, the short-term noise level was fairly independent of solvent flow rate and was not significantly increased at low flow rates as has been reported by Wilson and Cochrane[5]. Detector baseline instability was observed at flow rates of 2 to 4 cc/min., however. Optimum performance is therefore obtained with flow rates of 0.3 to 0.6 cc/min.

Selectivity of response to nitrogen compounds is primarily dependent upon the abstraction efficiency of the strontium hydroxide scrubber. Selectivity to nitrogen relative to chlorine, sulfur and esters is reported in Table XXXI. Selectivities in this table were calculated on the basis of the response per gram of nitrogen relative to the response per gram of an element or functional group using peak areas.

A mixture comprised of m-chlorotoluene (1 μg), thioansiole (1 μg), m-tolunitrile (10 ng), and methyl o-tolunate (1 μg) was used to determine selectivities. The quartz reaction tube contained a nickel catalyst made of a sufficient number of strands of 0.01-in. x 1.5 in. nickel wire so that it fit securely in the tube. The catalyst bed was positioned in the center of the hot zone. A strontium hydroxide scrubber (10% on glass wool) approximately 0.5 in. long was positioned in the tube just inside the end plate of the furnace.

Table XXXI. Selectivity to Nitrogen Relative to Halogen, Sulfur and the Ester Function[a,b].

| Group | Selectivity |
|---|---|
| Cl | >12,870 |
| S | 330 |
|  $-\overset{O}{\overset{\|}{C}}-O-R$ | > 1,700 |

[a] Conditions: Furnace, 800°; $H_2$ flow rate, 100 cc/min; solvent, 15% isopropyl alcohol at 0.4 cc/min.

[b] Selectivities calculated from peak areas.

No response was observed for m-chlorotoluene or methyl o-toluate, which results in selectivities for nitrogen relative to chlorine and the ester function of >12,870 and >1,700, respectively. A significant response was observed for 1 μg of thioanisole, and selectivity to nitrogen relative to sulfur is only 330. Selectivity to nitrogen relative to hydrocarbons, estimated from the response to the hexane solvent, is approximately $10^5$ to $10^6$.

"Reduction of Peak Tailing and Baseline Noise." Peak tailing in the nitrogen mode is usually due to insufficient basicity of the conductivity solvent or a badly contaminated scrubber. Peak tailing due to insufficient basicity is readily recognized by a sharp dip in the baseline just prior to the peak followed by a negative dip after the peak that gradually increases to the baseline (see Figure 46). The peak may be totally negative if the solvent is acidic or the quantity of nitrogen compound is small. Peak tailing due to contamination merely exhibits a trailing positive response. A contaminated catalyst can also result in peak tailing similar to that exhibited by a contaminated scrubber. Baseline noise is usually a result of the conductivity solvent or a leak in the system.

Peak tailing and baseline noise are usually eliminated by using 15% isopropyl alcohol as the conductivity solvent, an ion exchange tube packed with Amberlite IRN-150 and Duolite ARA-366 ($OH^-$ form), the addition of a small quantity of $N_2$ to the reaction gas (if required) and routine maintenance of the catalyst, solvent, ion exchange tube and scrubber. If the solvent is vented, the catalyst usually lasts for at least three to four months. The conductivity solvent should be replaced approximately every two weeks. The ion exchange resin normally lasts for approximately three to five months. The scrubber should be replaced as needed.

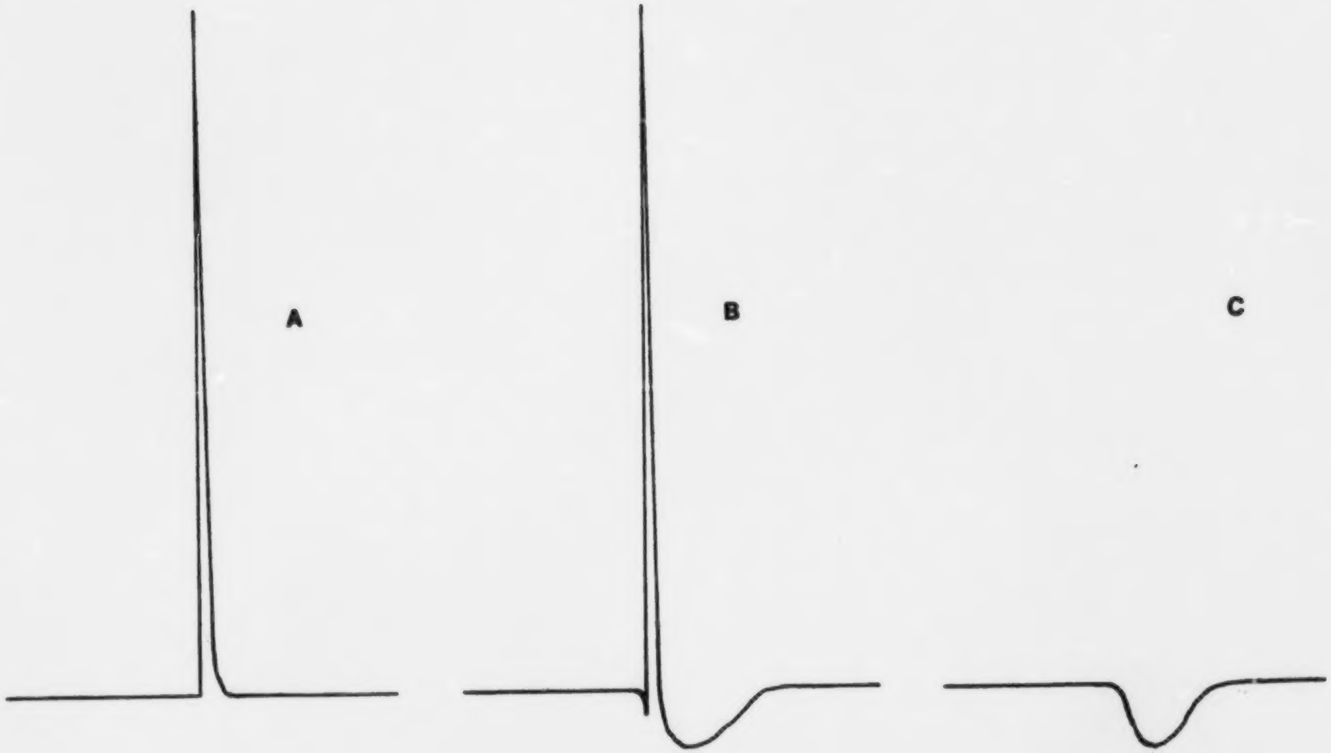


Figure 46. Peak shapes obtained for nitrogen-containing compounds: A, normal peak; B, peak obtained with an insufficiently basic conductivity solvent; C, peak obtained with an acidic conductivity solvent.

Linearity of Response to Nitrogen-Containing Compounds. Linearity of response at the lower end of the sensitivity range (0.1-10 ng) is dependent upon the basicity of the conductivity solvent. At a pH slightly above 7.0 response is very linear. However, if the conductivity solvent is acidic, linearity is very poor for lower sample quantities. Under normal operating conditions the detector displays a fairly linear response over approximately three to four orders of magnitude (0.1 ng - 1 μg). Response tends to level-off slightly at the upper concentration range, which may be due to swamping the catalyst or the solution chemistry of ammonia.

Detector linearity from 0.5 ng to 1 μg is shown in Figure 47 for CIPC and atrazine. Linearity from 1 ng to 1 μg is shown in Figure 48 for trifluralin, IPC and PCNB. Detector response at the nanogram level is plotted for CIPC, atrazine and simazine in Figure 49. These Figures show the excellent linearity that is displayed by the electrolytic conductivity detector for a variety of nitrogen-containing compounds.

Minimum Detectable Quantity. The minimum detectable quantity of nitrogen is primarily dependent upon polarity and correct basicity of the conductivity solvent. Optimum conditions for minimum detectability are the same as those for maximum linearity (15% isopropyl alcohol as the conductivity solvent and stacked IRN-150 and ARA-366 ion exchange resins). Minimum detectable quantities of 40 to 50 pg for atrazine and simazine at retention times of approximately 3 minutes can be routinely obtained. Minimum detectable quantities of a variety of nitrogen-containing pesticides are reported in Table XXXII. Chromatograms of low levels of nitrogen-containing pesticides are shown in Figures 50 and 51.

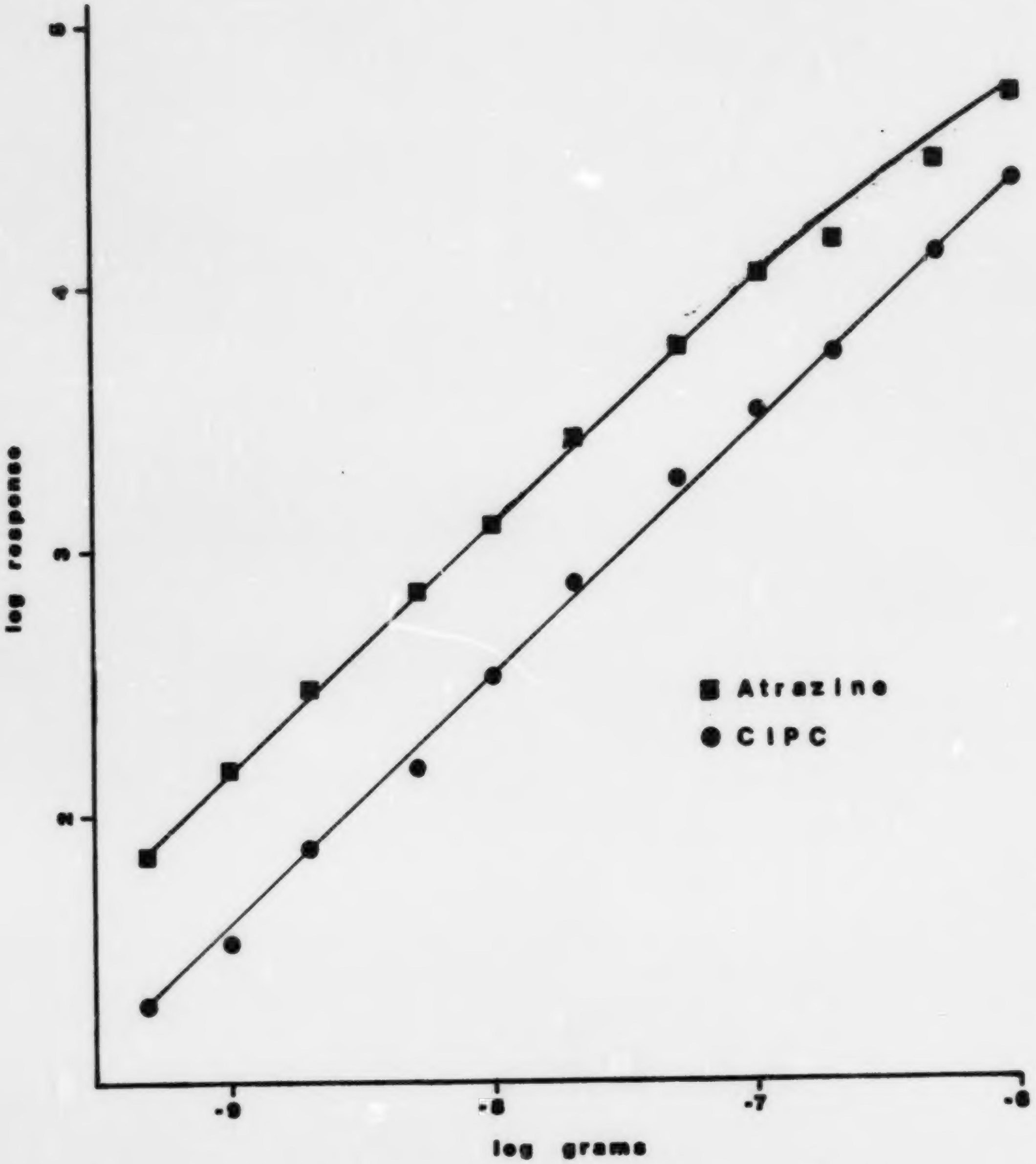


Figure 47. Linearity of response to atrazine and CIPC.

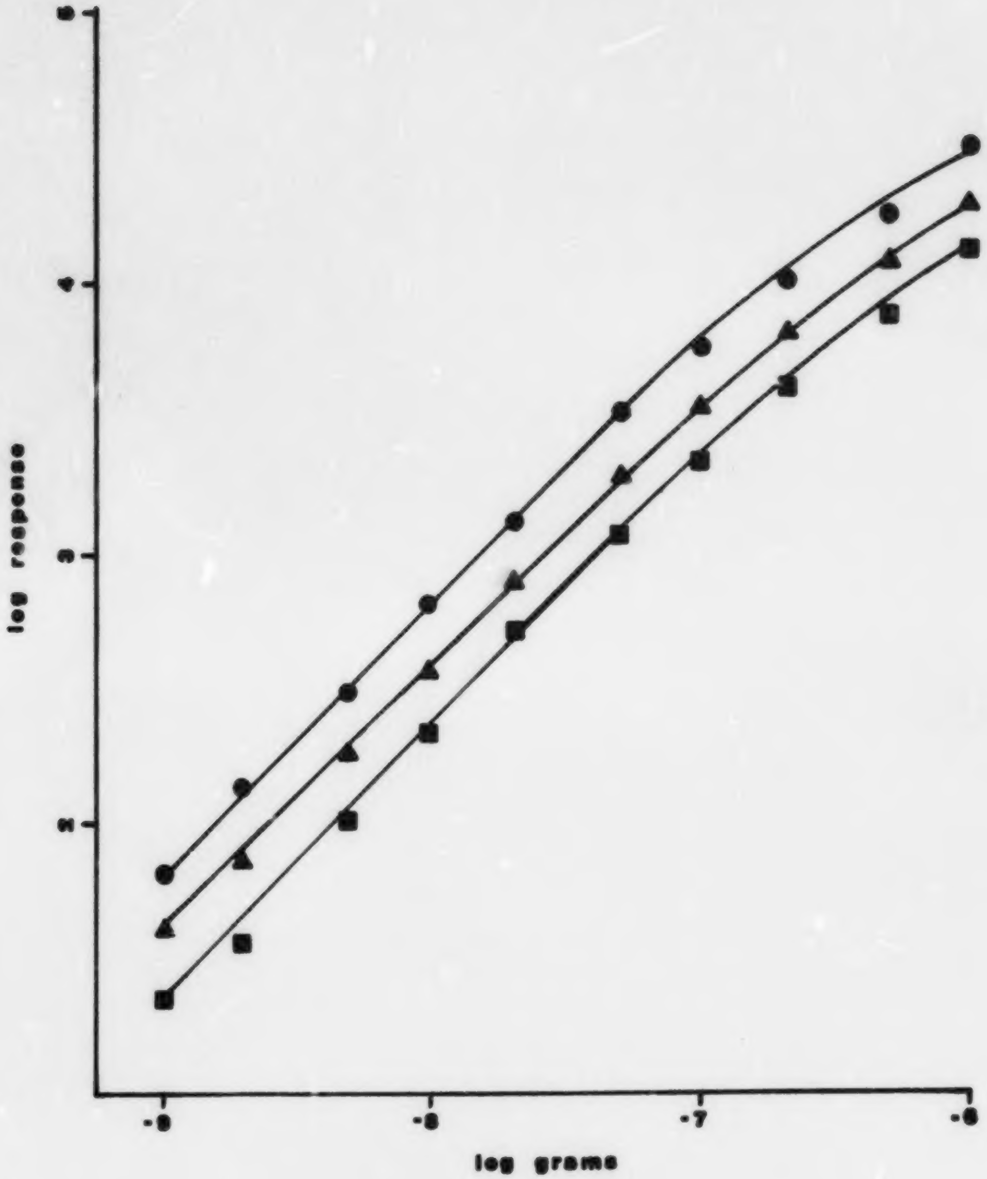


Figure 48. Linearity of response to trifluralin (●), IPC (▲) and PCNB (■).

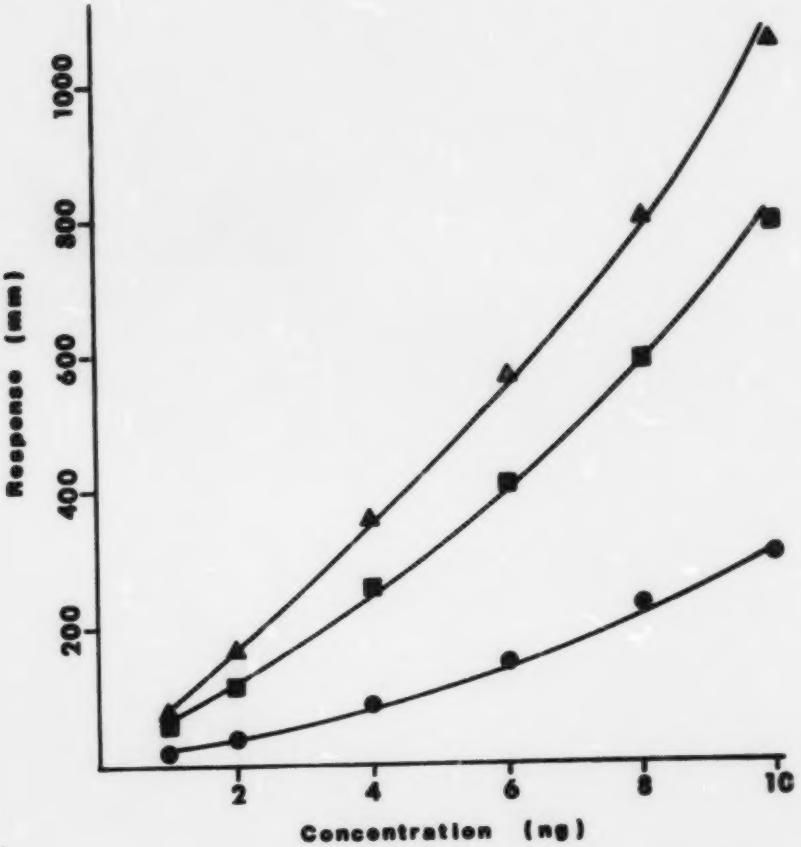


Figure 49. Linearity of response to CIPC (●), atrazine (▲), and simazine (■) from 1 to 10 ng.

Table XXXII. Minimum Detectable Quantities of Various Nitrogen-Containing Compounds[a].

| Conditions | Compound | | | | | |
|---|---|---|---|---|---|---|
| | Trifluralin | CIPC | IPC | PCNB | Atrazine | Simazine |
| 10% Isopropyl alcohol<br>1/3 IRN-150 + 2/3 IRN-78<br>FT = 800°, $H_2$ = 80 cc<br>Quartz tube with<br>nickel catalyst | 110pg<br>(0.96)[b] | 140pg<br>(1.52) | 190pg<br>(1.60) | 400pg<br>(2.00) | 37pg<br>(2.16) | 33pg<br>(2.88) |

[a] Minimum detectable quantities are 2x noise and short-term drift.

[b] Values in parenthesis are retention times in minutes.

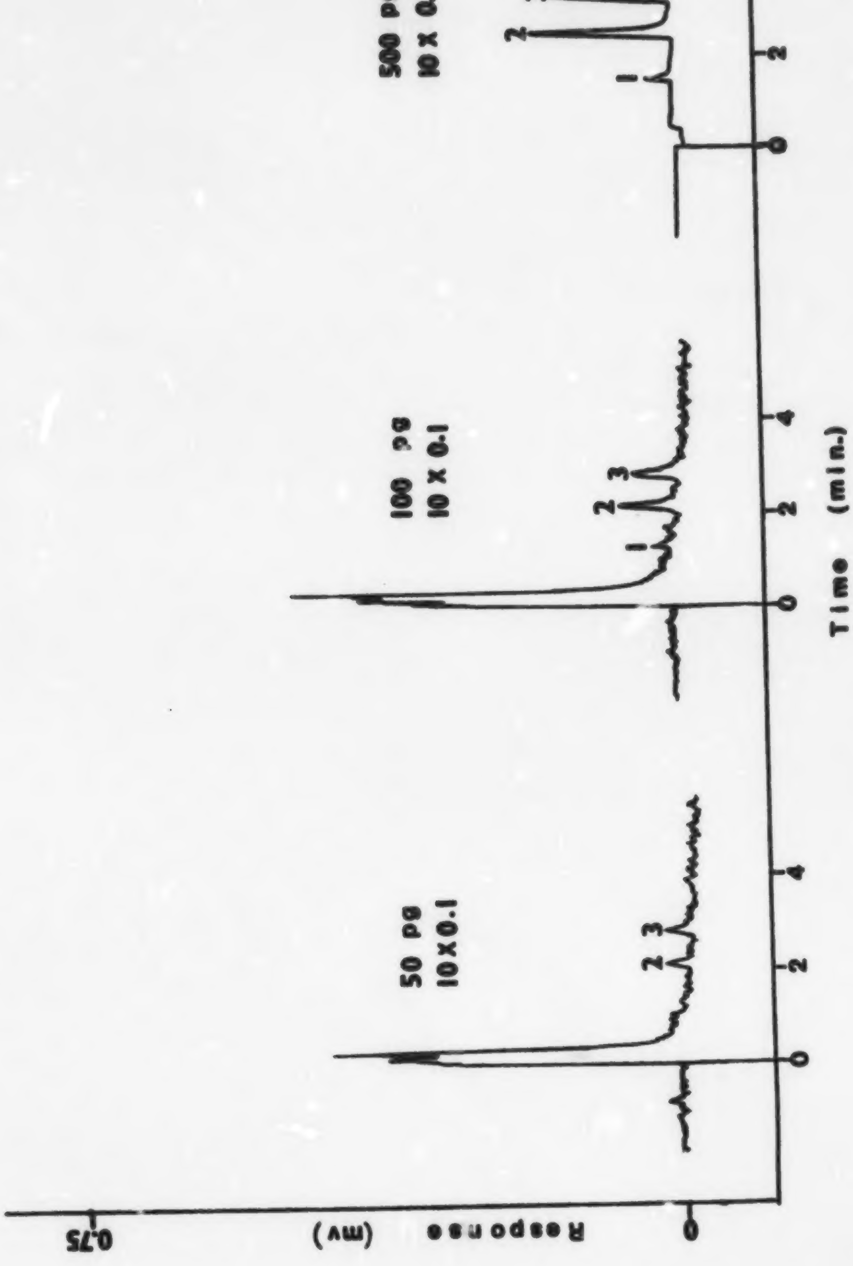


Figure 50. Chromatograms of low levels of CIPC (1), atrazine (2) and simazine (3).

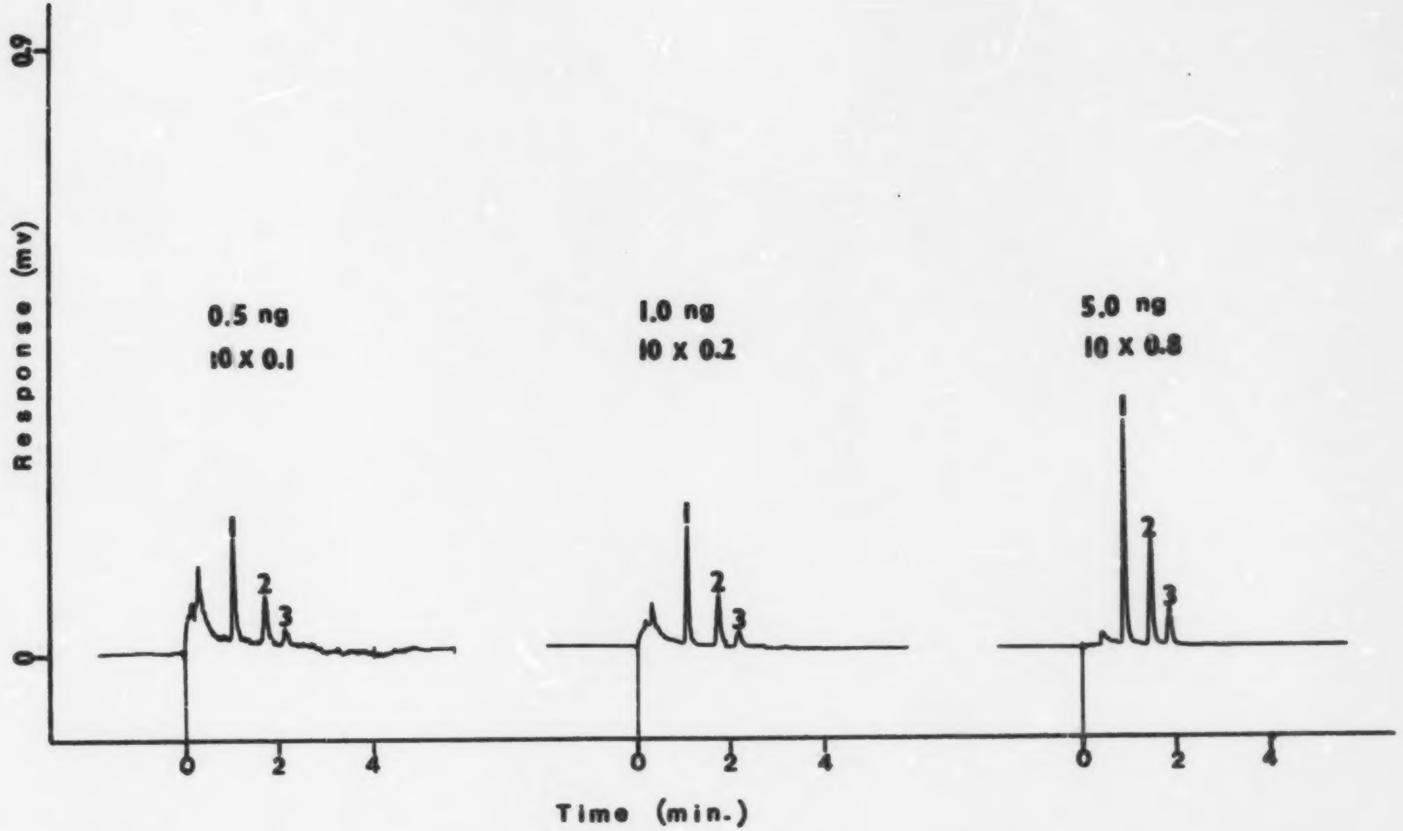


Figure 51. Chromatograms of low levels of trifluralin (1), IPC (2) and PCNB (3).

# APPLICATIONS

Detector utility for the determination of trace quantities of halogen-, sulfur- and nitrogen-containing compounds was evaluated for a wide variety of compounds and sample types. The primary objectives of this study were to determine the degree of interference from co-extracted naturally occuring and laboratory introduced contaminants and to ascertain the influence of these contaminants on detector response in the different modes of operation. Attempts were made to conduct this evaluation under similar analytical situations. Thus when possible, the same extraction procedure and chromatographic conditions were used so that interference in the various modes of operation could be directly compared. Consequently, the procedures used do not necessarily represent the best procedure for a given compound, but do represent general procedures that provide adequate performance. Also, attempts were not made to optimize recoveries since that was not the objective of this study.

This evaluation was complicated by the general lack of information regarding extraction and cleanup procedures for many of the compounds studied. The large number of operation parameters studied and the need to investigate numerous cleanup procedures for soil and biological extracts often required amendments in analytical methodology to be made in "mid-stream" in order for the study to be completed in the short time available. For instance, paraffin oil was used as a "keeper" for the analysis of sulfur compounds in the pyrolytic mode, but mineral oil was found to slowly "poison" the nickel catalyst in the determation of nitrogen compounds in the catalytic reductive mode and was thus deleted for nitrogen compounds.

## Analysis of Chlorine-Containing Pesticides in the Presence of PCB and PCN in Water Soil and Biological Samples.

Chlorinated hydrocarbon pesticides were analyzed in the presence of PCB and PCN with the detector operated in the catalytic oxidative mode for water and fat samples, and in the pyrolytic mode for soil samples. A 0.02 in. i.d. nickel reaction tube and methyl alcohol conductivity solvent were used for the catalytic oxidative mode; and a 2 mm i.d. quartz reaction tube and ethyl alcohol were used for the pyrolytic mode. Furnace temperatures and reaction gas flow rates are described under specific analyses.

Analysis of Chlorine-Containing Pesticides in Water. Water samples (500 ml) were fortified by the addition of 1.0 ml of an ethanolic solution of pesticides (lindane, heptachlor, aldrin, heptachlor epoxide and dieldrin), PCB (Aroclor 1254) and PCN (Halowax 1013). The PCB and PCN concentrations were always 10x that of the individual pesticides. The water samples were extracted 3x with 10 ml of 1:3 ether/hexane and the extracts combined. The combined extracts were dried with approximately 1 g of $Na_2SO_4$, and then reduced in volume to near dryness. The reduced extract was quantitatively transferred to a 15-ml culture tube with approximately 5 ml of hexane. The transferred extract was evaporated at room temperature with a gentle stream of dry air. A Florisil trap was used to remove any impurities from the air stream. The extracts were dissolved in hexane (1.0 or 10.0 ml) for gas chromatographic analysis.

The extracts were analyzed with a furnace temperature of $800^{\circ}$ and 100 cc/min of air reaction gas. Recoveries of the pesticides at 100 ppt, 400 ppt, 1 ppb and 10 ppb are summarized in Table XXXIII. Representative chromatograms of the extracts are shown in Figure 52. Recoveries ranged from a low of 62% for heptachlor at 100 ppt to a high of 110% for heptachlor epoxide at 100 ppt

Table XXXIII. Recovery of Chlorinated Hydrocarbon Pesticides from Water in the Presence of PCB and PCN[a].

| Pesticides | % Recovery[b] | | | |
|---|---|---|---|---|
| | 100 ppt | 400 ppt | 1 ppb | 10 ppb |
| Lindane | 70 | 84 | 73 | 71 |
| Heptachlor | 62 | 81 | 72 | 71 |
| Aldrin | 83 | 73 | 82 | 73 |
| Hept. epox. | 110 | 107 | 91 | 86 |
| Dieldrin | 98 | 90 | 99 | 87 |

[a] Water samples contained PCB and PCN in a 10-fold excess.

[b] Recoveries are the average of three replicates.

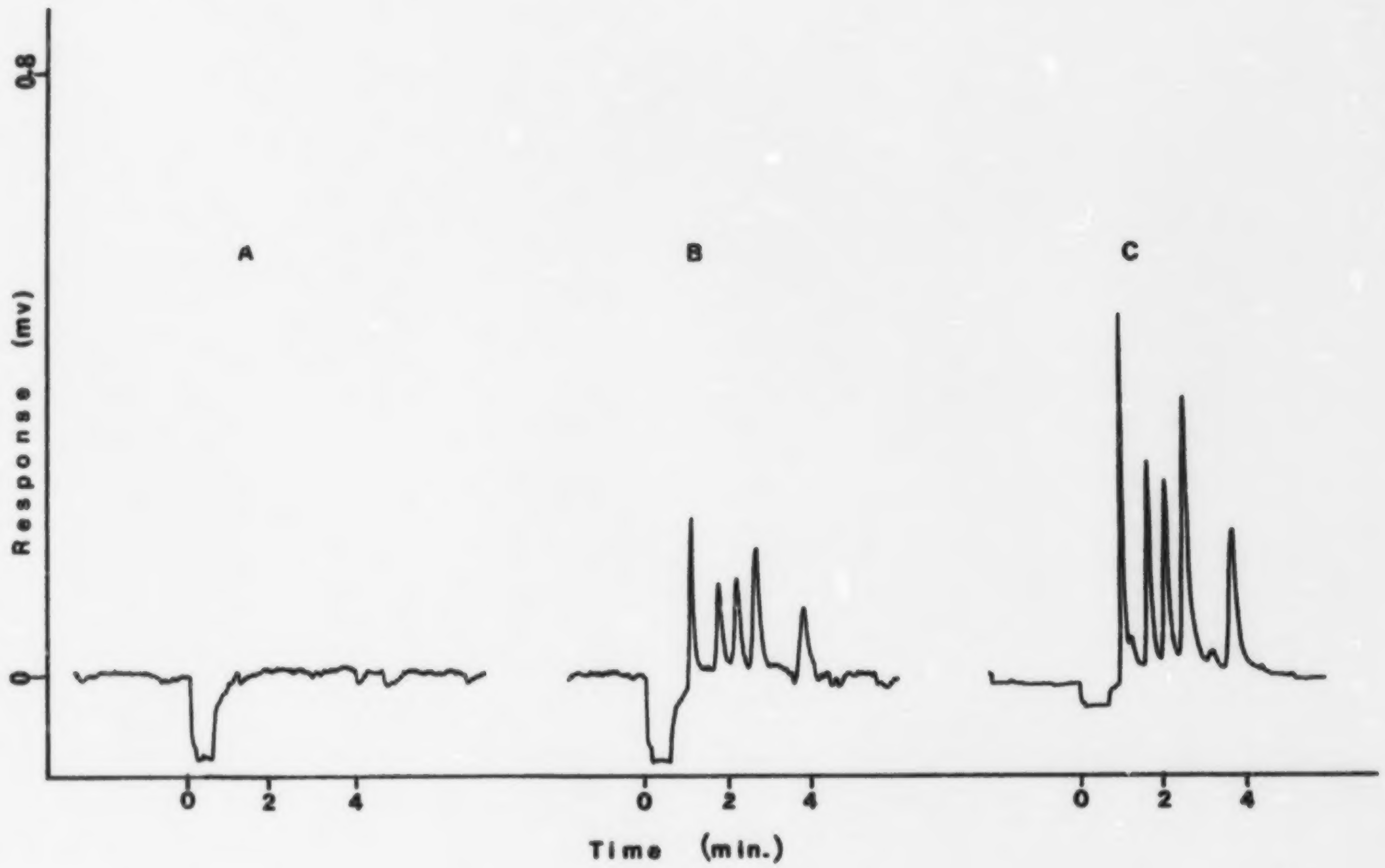


Figure 52. Chromatograms of chlorinated pesticides extracted from water. Sample: A, control, attenuation = 1 X 0.4; B, 100 ppt, attenuation = 1 X 0.4; C, 1 ppb, attenuation = 1 X 1.6.

Heptachlor epoxide and dieldrin consistently gave the highest recoveries, whereas lindane and heptachlor usually gave the lowest recoveries. Since lindane and heptachlor are the most volatile and gave the lowest recovery, there may have been some loss of these pesticides due to their volatility.

The mean recovery for the five pesticides at the four concentration levels was 83% with a standard deviation of 13.1. This recovery is good when it is considered that the analyses were conducted in the presence of a large excess of PCB and PCN. The average recovery and standard deviation could probably be improved by using more elaborate techniques of solvent evaporation.

Analysis of pesticides in samples that contain PCB and PCN by classical techniques using electron capture detection requires the physical isolation of the pesticides by column chromatography. In our hands, this was found to require initial separation on a Florisil column followed by further isolation on coconut charcoal and silica gel columns. Overall recoveries by these techniques were found to be quite low and varied considerably. Also, separation of some pesticides from PCB and PCN by multiple column chromatography is not complete. Thus, the analysis of pesticide-PCB-PCN mixtures by selective detection is considerably easier and usually gives as good or better results.

Analysis of Chlorine-Containing Pesticides in Soil. Soil samples (25 g) were fortified with 1.0 ml of a hexane solution of pesticides (lindane, heptachlor, aldrin, heptachlor epoxide and dieldrin), PCB (Aroclor 1254) and PCN (Halowax 1013). The PCB and PCN concentrations were 10x the level of the individual pesticides. The soil samples contained in 250 ml erlenmeyer flasks, were wetted with 5 ml of water and extracted by shaking with 100 ml of 1:1

hexane/isopropyl alcohol on a wrist-action shaker for 15 min. The extract was filtered through Whatman 2-V fluted filter paper. The flask was rinsed with an additional 10 ml of solvent, which was also used to wash the filter paper. The filtrate was then reduced to near dryness on a rotary evaporator. The reduced extract was quantitatively transferred to a culture tube (15 ml) with approximately 5 ml of hexane. The extract was evaporated with a gentle stream of air, and the remaining residue dissolved in hexane (1.0 or 10 ml) for gas chromatographic analysis.

The extracts were analyzed using a furnace temperature of $700^0$ and a hydrogen reaction gas flow rate of 2 cc/min. Recoveries of the pesticides at 0.01 ppm, 0.1 ppm, 1.0 ppm and 10.0 ppm are presented in Table XXXIV. Representative chromatograms of the soil extracts are reproduced in Figures 53-55. Recoveries at 0.1, 1.0 and 10.0 ppm were good and ranged from 74 to 98% with a mean (for all the pesticides) of 85% and a standard deviation of 6.5. Recoveries of the more volatile pesticides tended to be a little lower than the less volatile ones. However, this difference was lower than in the water analysis. The extracts contained some residue from the soil which could have minimized loss due to volatilization.

Although the recoveries at 0.1, 1.0 and 10.0 ppm were good and the pesticides could easily be analyzed in the presence of an excess of PCB and PCN 10x that of the individual pesticides, recoveries at the 0.01 ppm level were low, with the exception of dieldrin. The extracts contained a number of small peaks at the retention times of the first four pesticides. The intensity of these peaks was variable and thus the substraction of their response from that of the pesticides resulted in variable and low recoveries for these compounds. These impurities were not removed by a Florisil cleanup column. Thus, the lower level of analysis for these particular samples is estimated to be approximately 0.03 ppm.

Table XXXIV. Recovery of Chlorinated Hydrocarbon Pesticides from Soil in the Presence of PCB and PCN[a].

| Pesticide | % Recovery[b] | | | |
|---|---|---|---|---|
| | 0.01 ppm | 0.1 ppm | 1.0 ppm | 10.0 ppm |
| Lindane | 37 | 85 | 78 | 79 |
| Heptachlor | 42 | 84 | 74 | 86 |
| Aldrin | 53 | 98 | 79 | 81 |
| Hept. epox. | 65 | 90 | 84 | 87 |
| Dieldrin | 85 | 96 | 85 | 85 |

[a] Samples contained PCB and PCN in a 10-fold excess.

[b] Recoveries are the average of three replicates.

[c] Sample contained 50 g of soil.

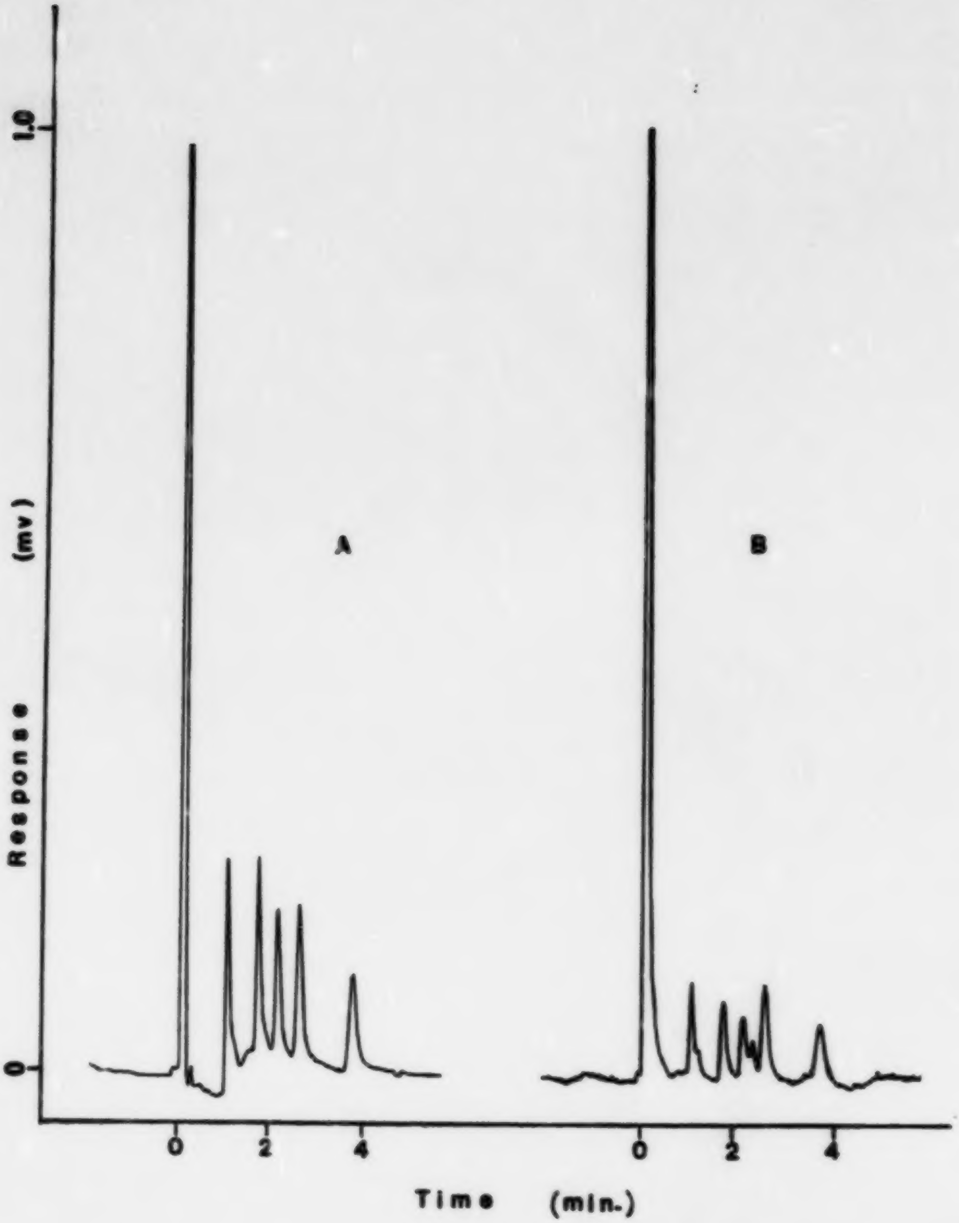


Figure 53. Chromatograms of chlorinated pesticides extracted from soil. Sample: A, 2.5 ng of pesticides, attenuation = 1 X 1.6; B, 0.01 ppm, attenuation = 1 X 1.6.

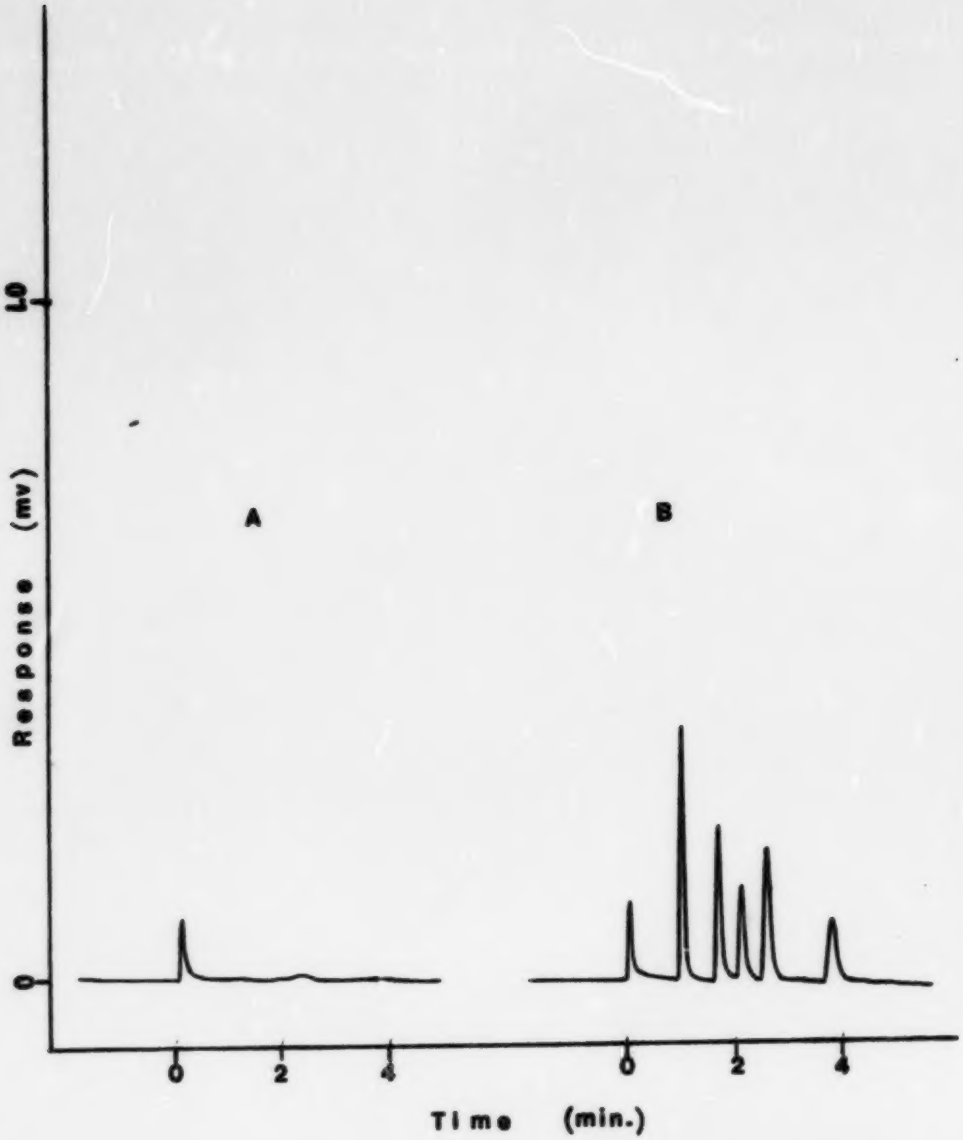


Figure 54. Chromatograms of chlorinated pesticides extracted from soil. Sample: A, control, attenuation = 10 X 0.2; B, 0.1 ppm, attenuation = 10 X 0.2.

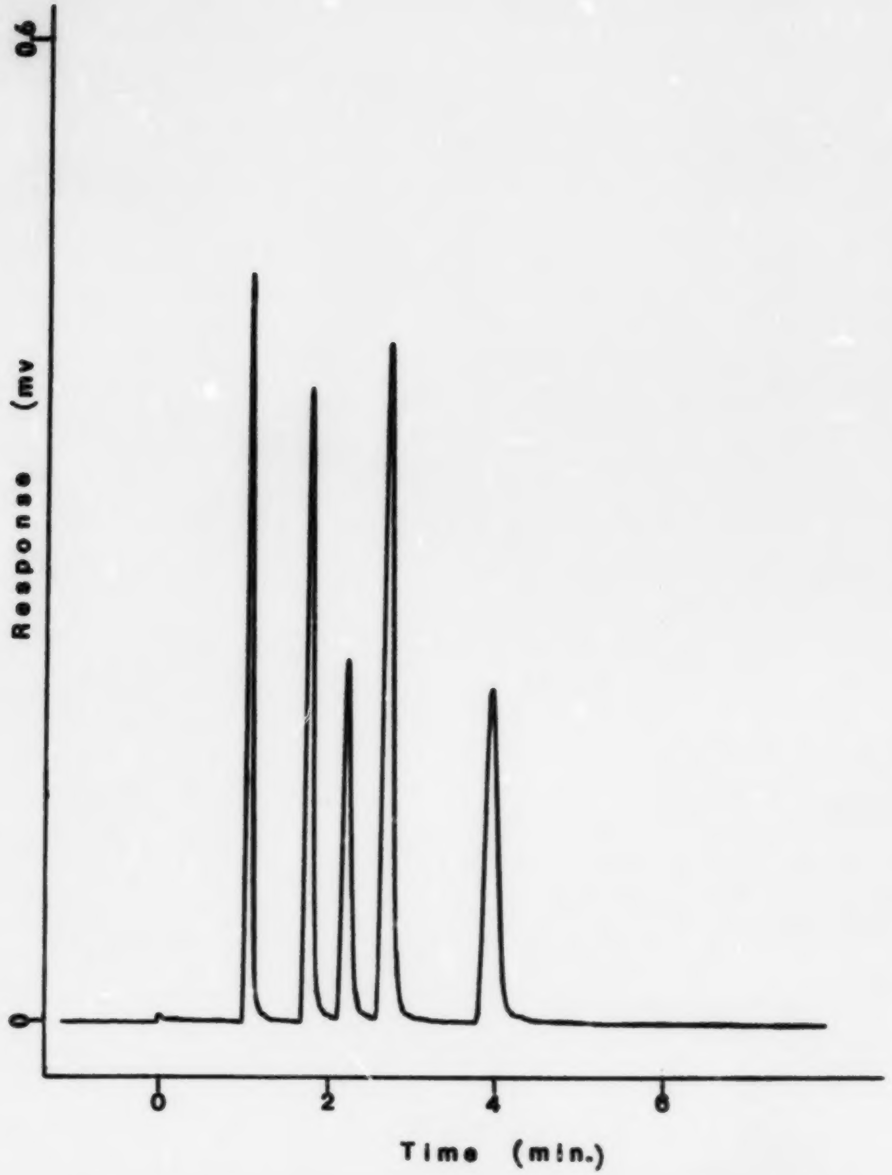


Figure 55. Chromatogram of soil extract fortified with 1 ppm of chlorinated pesticides. Attenuation: 10 X 3.2.

Analysis of Chlorine-Containing Pesticides in Fat Samples. The analysis of chlorinated hydrocarbon pesticides in fat was attempted with fish fat, lard, and chicken fat. Hexane extracts of fat (10 g) were fortified with pesticides (lindane, heptachlor, aldrin, heptachlor epoxide and dieldrin), PCB (Aroclor 1254) and PCN (Halowax 1013). The PCB and PCN concentrations were 10x that of the pesticides. Separation of the pesticides from the lipids was attempted by liquid-liquid partitioning followed by a Florisil cleanup as described in Section 5,A,(1) of the EPA "Manual of Analytical Methods", Research Triangle Park, NC. Separation of the pesticides from the lipids was also attempted by liquid-liquid partitioning with hexane and 95% methyl alcohol. In all cases, a considerable amount of fat (approximately 0.25-1 g) remained in the final extract. The acetonitrile/hexane Florisil column procedure was also used for 1-g fat samples.

The extracts were dissolved in hexane (1.0 to 10.0 ml) and analyzed using a furnace temperatures of 700 to 750$^0$ and hydrogen reaction gas flow rates of 0 to 5 cc/min. However, analysis was unsuccessful. After approximately five to six injections, detector sensitivity and peak shape deteriorated to such an extent that quantitation was impossible (see Figure 56). Analysis was also attempted with a nickel reaction tube operated in the catalytic oxidative mode at a furnace temperature of 780$^0$ (selective to aliphatic chlorine). The same results were obtained, however.

Sensitivity and peak shape were partially restored by changing the reaction tube, but they were not fully restored until the column and transfer lines were cleaned. The inlet side of the column had a dark brown residue (after approximately 30 injections), which required replacing the first 6 in. of column packing. It can thus be concluded, that the analysis

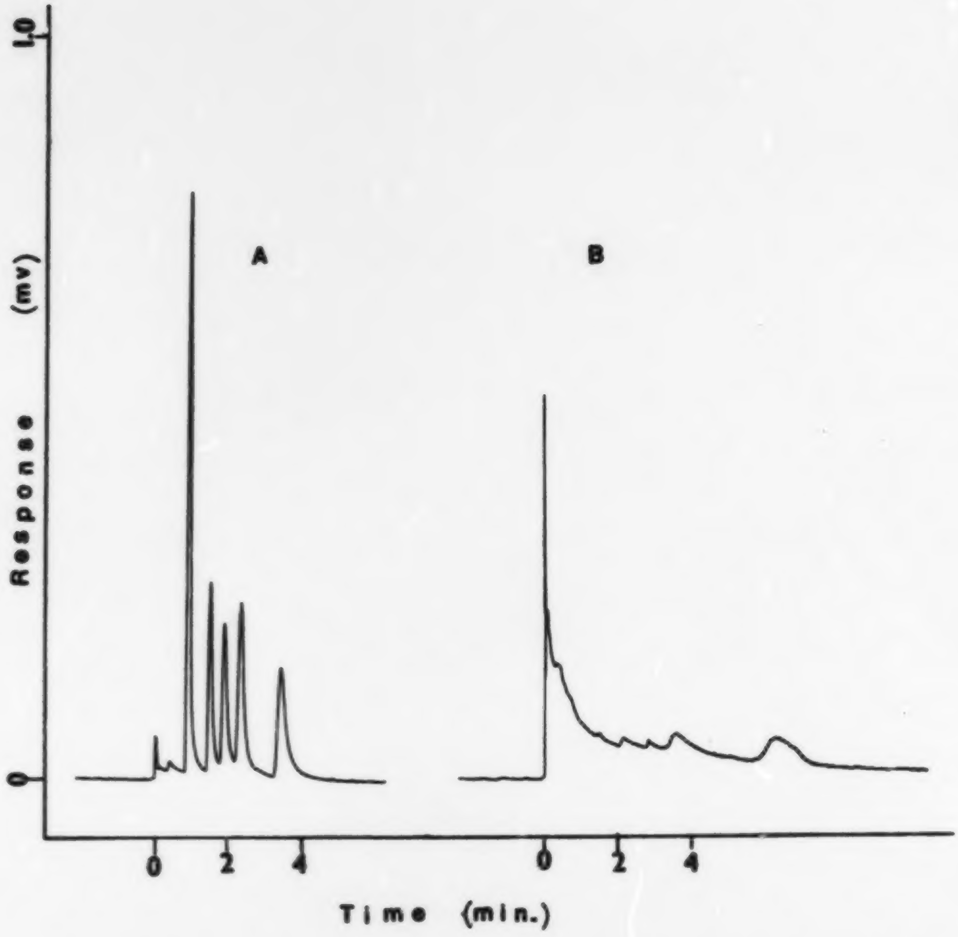


Figure 56. Chromatograms of the chlorinated pesticide mixture before and after the injection of fat extracts. , Sample: A, 2.5 ng of chlorinated pesticides prior to injection of fat extracts; B, 2.5 ng of chlorinated pesticides after the injection of approximately 20 extracts.

of lipid extracts is not feasible until more effective cleanup techniques are developed. Although the cleanup procedures employed may be sufficient for the analysis of dilute sample extracts by electron capture detection, they are not adequate for the determination of the fairly concentrated lipid samples required with the electrolytic conductivity detector.

### Analysis of Sulfur-Containing Pesticides in Water, Soil and Biological Samples.

Sulfur-containing pesticides in water and alfalfa were analyzed with the detector operated in the catalytic oxidative mode. A 0.02-in. i.d. nickel reaction tube, 100 cc/min. of air reaction gas, and methyl alcohol conductivity solvent were used. Sulfur-containing pesticides in soil were analyzed in the pyrolytic mode with a 1-mm i.d. quartz reaction tube packed with approximately 0.25 in. of quartz wool. Air at a flow rate of 20 cc/min. was used as the reaction gas and methyl alcohol as the conductivity solvent in the pyrolytic mode.

Analysis of Sulfur-Containing Pesticides in Water. Water samples (500 ml) were fortified by the addition of 1.0 ml of an ethanolic pesticide mixture. Three different pesticide mixtures were used. One mixture contained Thimet, malathion, captan, Thiodan I, Thiodan II and trithion. A second solution contained diazinon, methyl parathion and parathion. The third solution contained diallate. The water samples were extracted as described for the analysis of chlorine containing pesticides in water.

The extracts were analyzed with the detector operated at 650$^{\circ}$. Recoveries of the pesticides at 100 ppt, 400 ppt, 1 ppb and 10 ppb are reported in Table XXV. Representative chromatograms of water extracts are exhibited

Table XXXV. Recovery of Sulfur-Containing Pesticides for Water.

| Pesticides | % Recovery[a] | | | |
|---|---|---|---|---|
| | 100 ppt | 400 ppt | 1 ppb | 10 ppb |
| Diallate | 78 | 88 | 73 | 81 |
| Diazinon | 96 | 83 | 70 | 87 |
| Methyl Parathion | 110 | 96 | 98 | 91 |
| Parathion | 96 | 113 | 80 | 90 |
| Thimet | 67 | 69 | 70 | 79 |
| Malathion | 76 | 72 | 86 | 87 |
| Captan | 65 | 79 | 99 | 91 |
| Thiodan I | 77 | 83 | 117 | 79 |
| Thiodan II | 93 | 77 | 102 | 75 |
| Trithion | 77 | 80 | 91 | 89 |

[a] Recoveries are the average of three replicates.

in Figures 57-59. The ten pesticides were recovered at the four concentration levels with an overall mean of 85% and a standard deviation of 12.4. The lowest recoveries were obtained for Thimet and captan, which can possibly be attributed to the volatility of Thimet and the poor chromatography of low quantities of captan. Recoveries, however, showed as much variability between concentration as they did between pesticides. This indicates that minor variations in technique such as evaporation time, evaporation temperature, and surface activity of the evaporation vessel may be more important than the individual pesticides analyzed. Nevertheless, as shown in Figures 58 and 59, the electrolytic conductivity detector can be used for the analysis of low concentrations of sulfur-containing pesticides in water.

During the course of this study, it was noticed that deionized water contained a moderately high level of numerous sulfur-containing compounds that exhibited detector responses equivalent to approximately 300 to 600 ppt of the sulfur pesticides. The removal of these impurities required careful distillation. Impurities in $Na_2SO_4$ also presented a problem, and required that the $Na_2SO_4$ be soxhlet extracted and heat treated at $180^o$ for 24 hr. Consequently, due care should be exercised in the analysis of trace quantities of pesticides in water.

Analysis of Sulfur-Containing Pesticides in Soil. Soil samples (25 g) were fortified with hexane solutions of the same three mixtures of pesticides as described for water analysis. The soil was fortified at levels of 0.01, 0.1, 1.0 and 10.0 ppm. The soil was extracted as described for the analysis of chlorinated hydrocarbon pesticides in soil, except 1 ml of 10% paraffin oil in hexane was added to the filtrate as a "keeper".

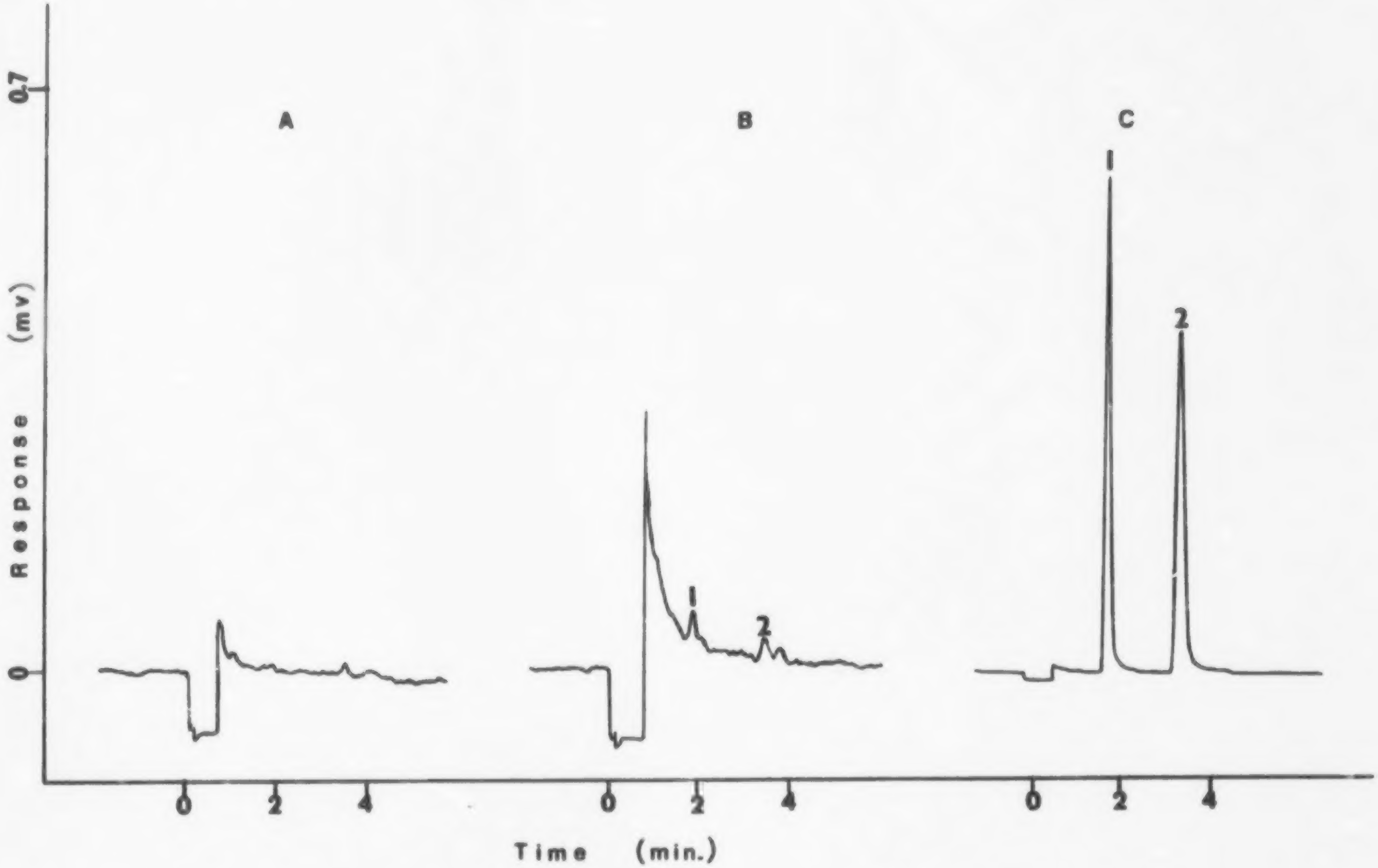


Figure 57. Chromatograms of diazinon (1) and parathion (2) extracted from water. Sample: A, control, attenuation = 1 X 0.2; B, 100 ppt, attenuation = 1 X 0.2; C, 1 ppb, attenuation = 10 X 0.2.

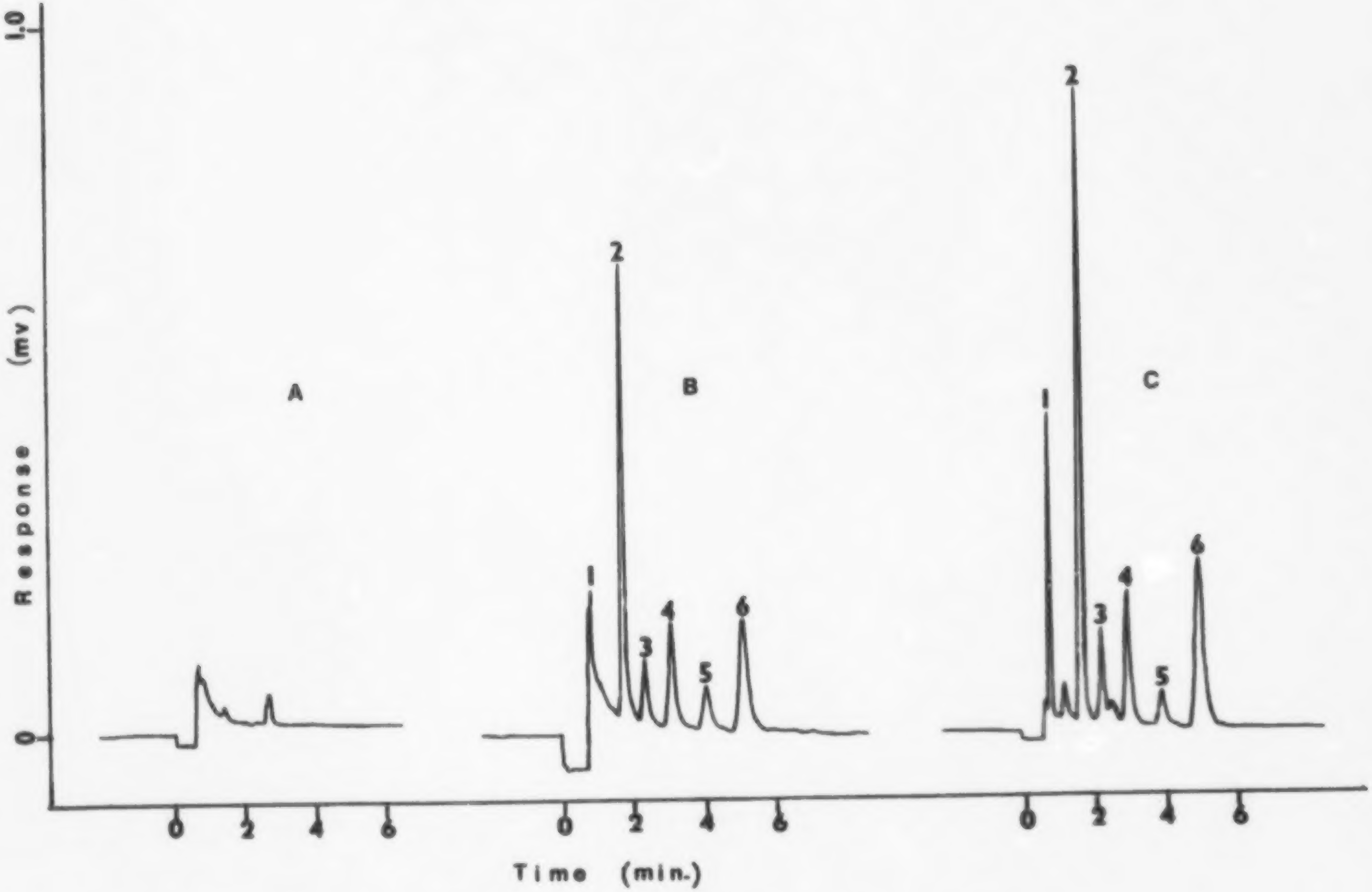


Figure 58. Chromatograms of Thimet (1), malathion (2), captan (3), Thiodan I (4), Thiodan II (5) and trithion (6) extracted from water. Sample: A, control, attenuation = 1 X 0.4; B, 100 ppt, attenuation = 1 X 0.4; C, 1 ppm, attenuation = 10 X 0.1.

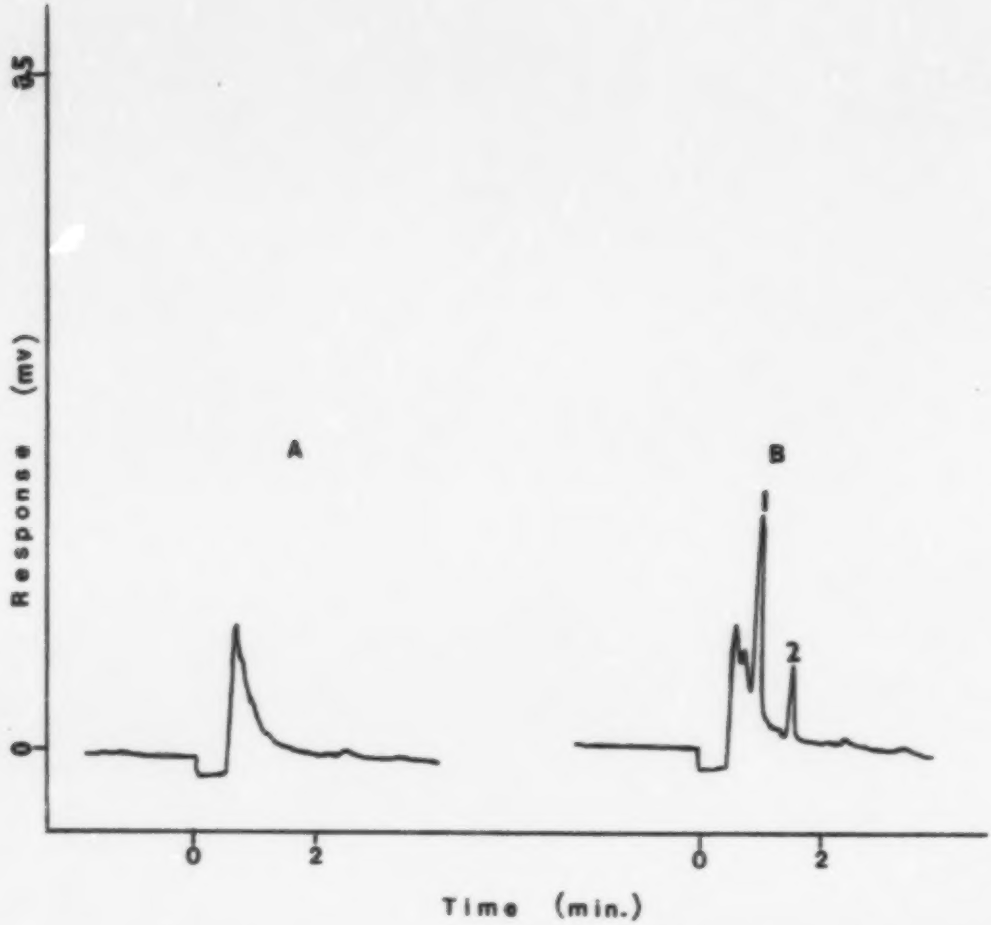


Figure 59. Chromatograms of diallate (1) and methyl parathion (2) extracted from water. Sample: A, control, attenuation = 1 X 0.4, B, 400 ppt, attenuation = 1 X 0.4.

Recoveries are displayed in Table XXXVI, and representative chromatograms of the analyses are shown in Figures 60-62. As shown by the data in this table, diazinon, methyl parathion, parathion and captan could not be determined at the 0.01 ppm level. The presence of contaminants and/or insufficient response precluded those particular analyses. The other pesticides were determined with excellent recoveries. The mean recovery for all analyses was 93% with a standard deviation of 10.3.

Attempts to remove sample interference with a Florisil cleanup column resulted in low and variable recoveries. Recoveries were not significantly improved by different elution solvents or different Florisil activities. Florisil activities that gave good recoveries failed to remove the sample impurities. A cleanup procedure was therefore not used. The sample extracts were distinctly yellow, and the reaction tube had to be cleaned and the quartz wool contact material replaced weekly.

Analysis of Sulfur-Containing Pesticides in Alfalfa. Alfalfa samples (10 g) were fortified with a hexane solution of Thimet, malathion, Thiodan I, Thiodan II and trithion. Samples were fortified at 0.02, 0.1, 1.0 and 10.0 ppm. Samples were extracted by blending with acetonitrile (40 ml) for 2 min with a Sorvall omnimixer. The blender cup was rinsed with acetonitrile and the extract filtered. The filtrate was evaporated on a rotary evaporator until only a small aqueous residue was left. The residue was transferred to a separatory funnel with ether, approximately 5 ml of 10% aqueous NaCl added and extracted three times with 15 ml of ether. The ether was then evaporated, the residue dissolved in 2 ml of ether and quantitatively transferred to a 4:1 Florisil/Celite cleanup column that contained 10% water. The shell column was packed with 5 g of Florisil-Celite and contained 1 in. of $Na_2SO_4$

Table XXXVI. Recovery of Sulfur-Containing Pesticides from Soil.

| Pesticide | % Recovery[a] | | | |
|---|---|---|---|---|
| | 0.01 ppm | 0.1 ppm | 1.0 ppm | 10.0 ppm |
| Diallate | 88 | 100 | 95 | 101 |
| Diazinon | -- | 93 | 101 | 91 |
| Methyl Parathion | -- | 103 | 105 | 88 |
| Parathion | -- | 100 | 101 | 92 |
| Thimet | 78 | 95 | 100 | 89 |
| Malathion | 92 | 101 | 105 | 95 |
| Captan | -- | 95 | 71 | 89 |
| Thiodan I | 93 | 62 | 97 | 100 |
| Thiodan II | 94 | 63 | 98 | 101 |
| Trithion | 91 | 99 | 100 | 90 |

[a] Recoveries are the average of three replicates.

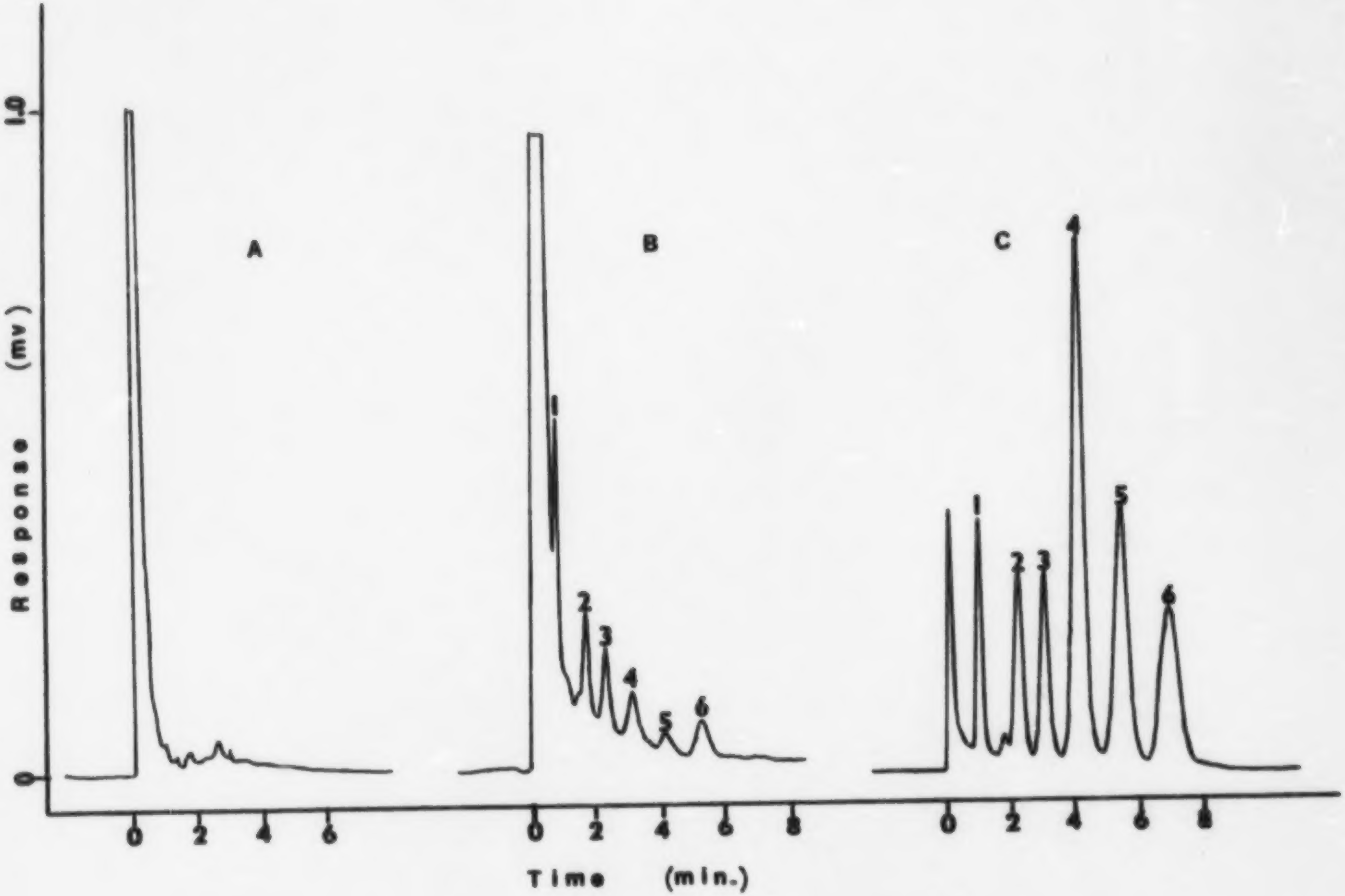


Figure 60. Chromatograms of Thimet (1), malathion (2), captan (3), Thiodan I (4), Thiodan II (5) and trithion (6) extracted from soil. Sample: A, control, attenuation = 1 X 1.6; B, 0.01 ppm, attenuation = 1 X 1.6, C, 1 ppm, attenuation = 10 X 3.2.

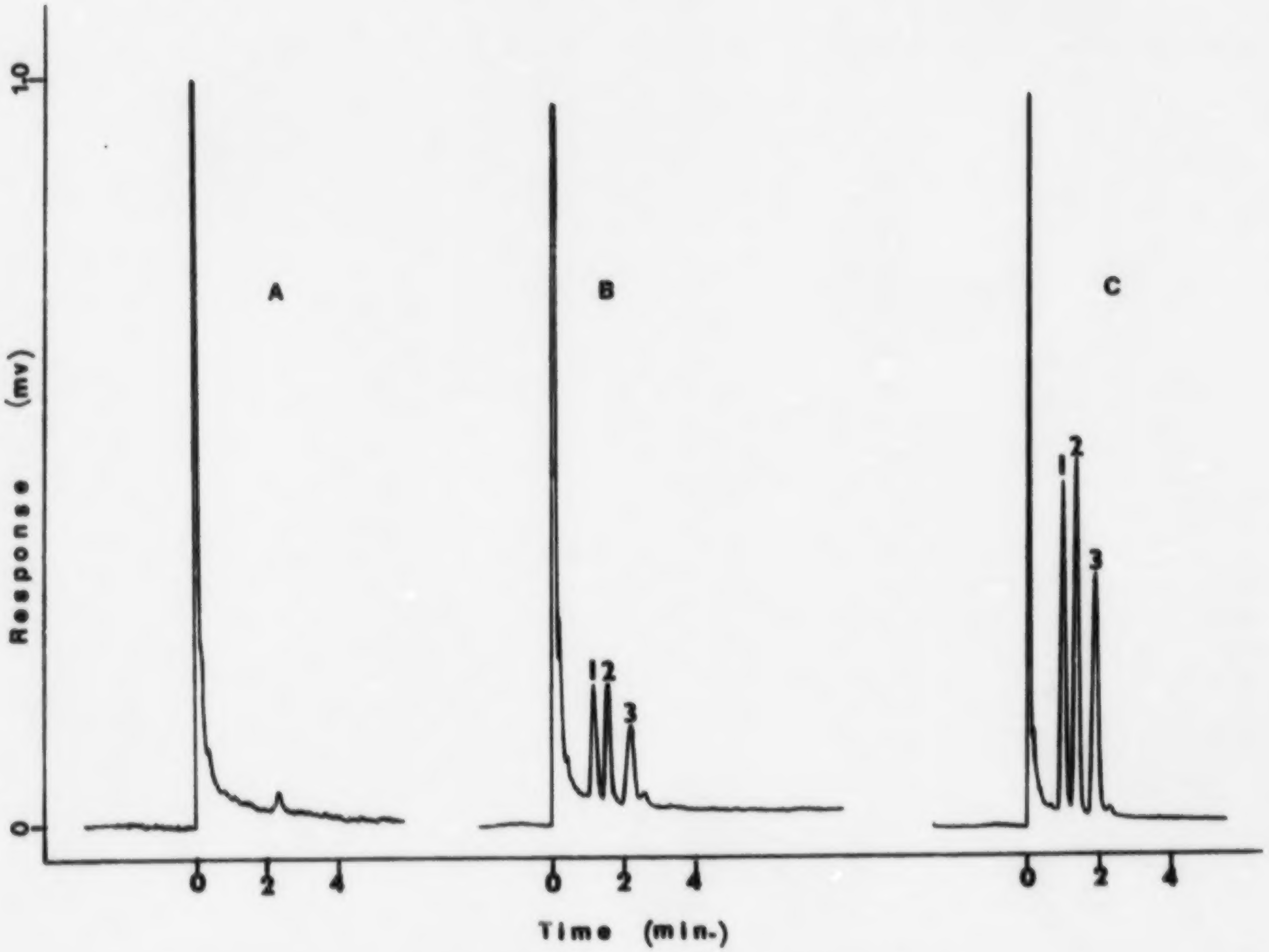


Figure 61. Chromatograms of diazinon (1), methyl parathion (2) and parathion (3) extracted from soil. Sample: A, control, attenuation = 1 X 1.6; B, 0.1 ppm, attenuation = 1 X 1.6; C, 1 ppm, attenuation = 1 X 3.2.

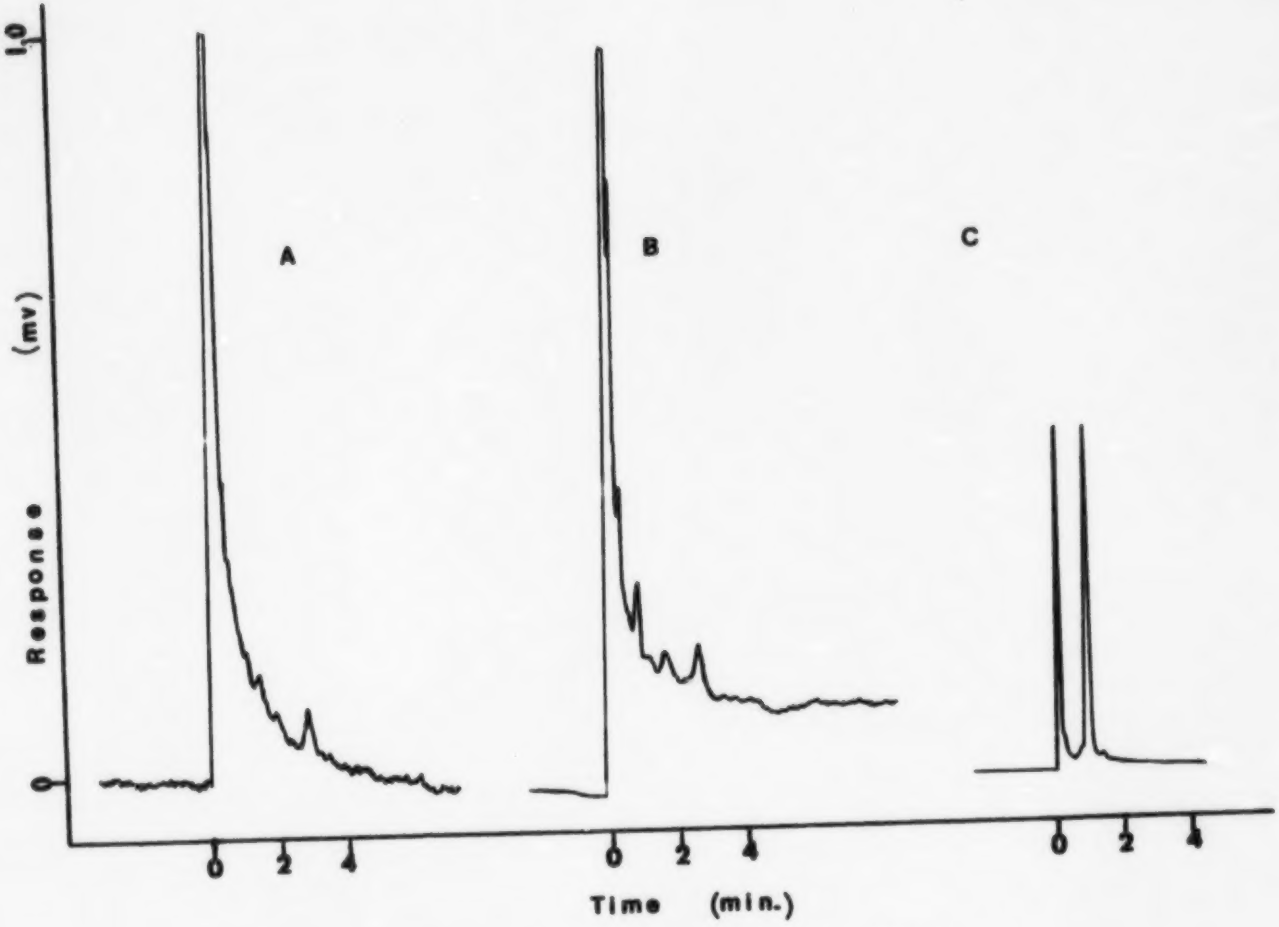


Figure 62. Chromatograms of diallate extracted from soil. Sample: A, control, attenuation = 1 X 1.6; B, 0.01 ppm, attenuation = 1 X 1.6; C ppm, attenuation = 10 X 1.6.

on the top and bottom. The column was washed with 10 ml of hexane prior to the addition of the extract, which was added to the column in 20 ml of 10% ether in hexane. The column was eluted with 100 ml of 10% ether in hexane. The eluate was evaporated to near dryness on a rotary evaporator, quantitatively transferred to a culture tube and evaporated to dryness with a dry, filtered stream of air. The residue was dissolved in hexane (1.0 to 10.0 ml) for chromatographic analysis.

Although the cleanup column effectively removed the chlorophylls and water soluble components, it did not remove the carotenoids and other oil soluble components. The purified extracts were dark yellow and exhibited a number of gas chromatographic responses that prevented analyses at the 0.01 ppm level. Liquid-liquid partitioning between acetonitrile and hexane reduced the intensity of the yellow color, but did not remove the interference. The interfering peaks also displayed the same response-furnace temperature relationship as the pesticides.

The extracts were analyzed in the catalytic oxidative mode at a furnace temperature of 860°. Recoveries of the pesticides are tabulated in Table XXXVII, and representative chromatograms of the extracts are shown in Figure 63. The pesticides were recovered with an overall mean of 85% and a standard deviation of 7.9.

The Florisil-Celite column was the only cleanup column investigated that provided adequate sample cleanup without pesticide loss. Other columns investigated included Florisil, alumina and silica gel of various activities. The alfalfa constituents that were not removed by the cleanup column did not appear to deteriorate sensitivity or peak shape.

Table XXXVII. Recovery of Sulfur-Containing Pesticides from Alfalfa.

| Pesticide | % Recovery[a] | | | |
|---|---|---|---|---|
| | 0.02 ppm | 0.1 ppm | 1.0 ppm | 10.0 ppm |
| Thimet | 87 | 87 | 75 | 72 |
| Malathion | 73 | 95 | 83 | 83 |
| Thiodan I | 83 | 86 | 87 | 91 |
| Thiodan II | 93 | 65 | 86 | 89 |
| Trithion | 87 | 95 | 88 | 88 |

[a] Recoveries are the average of three replicates.

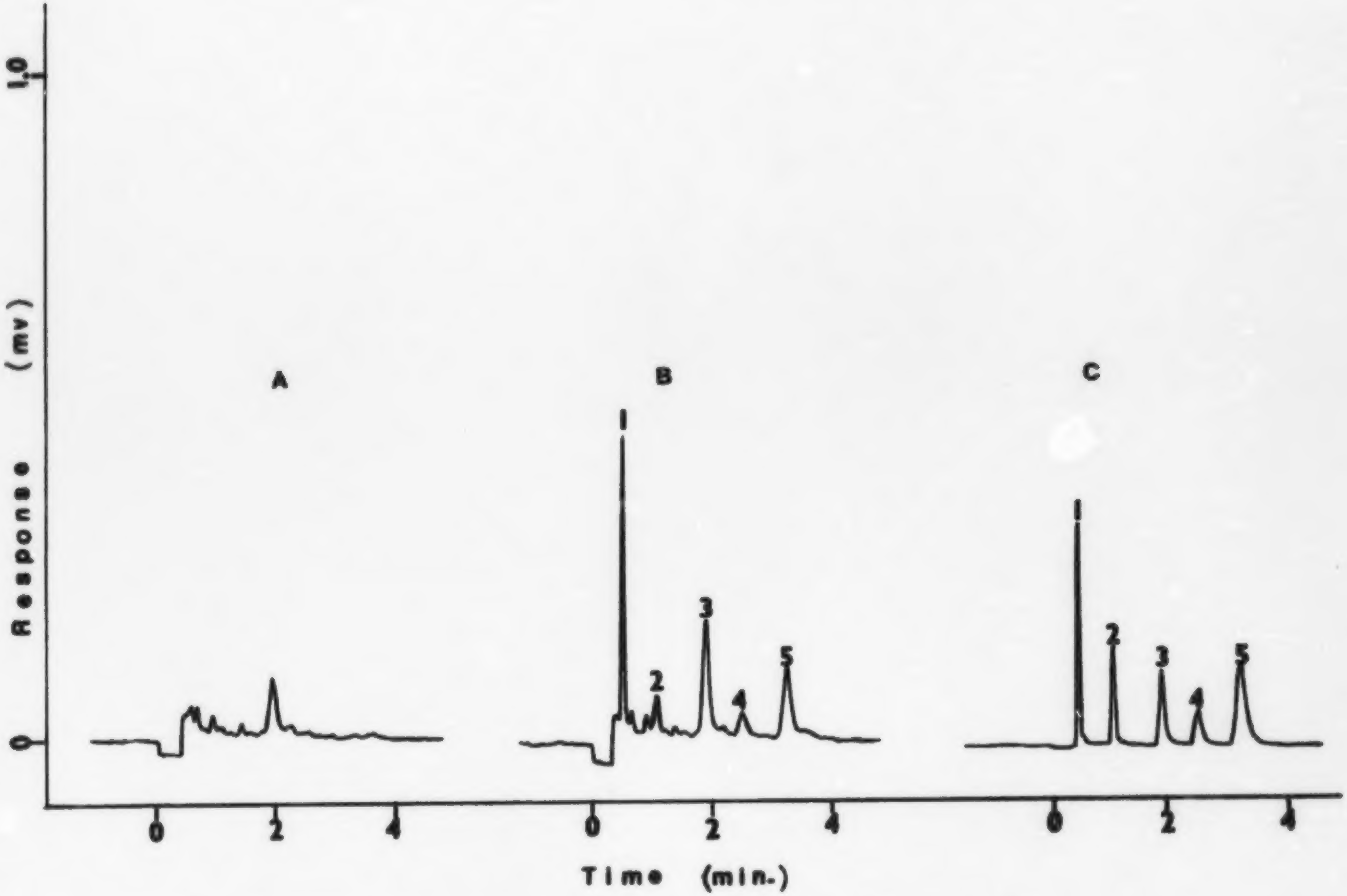


Figure 63. Chromatograms of Thimet (1), malathion (2), Thiodan I (3), Thiodan II (4), and trithion (5) extracted from alfalfa. Sample: A, control, attenuation = 1 X 0.8; B, 0.02 ppm, attenuation = 1 X 0.8; C, 1 ppm, attenuation = 10 X 0.2.

## Analysis of Nitrogen-Containing Pesticides in Water, Soil and Biological Samples.

Nitrogen-containing pesticides were analyzed in the catalytic reductive mode with a quartz reaction tube, nickel wire catalyst, 15% isopropyl alcohol conductivity solvent and a furnace temperature of 820°. A strontium hydroxide scrubber was placed in the quartz tube just within the furnace wall.

Analysis of Nitrogen-Containing Pesticides in Water. Water samples (1 l) were fortified at 100 ppt, 400 ppt, 1.0 ppb and 10 ppb by the addition of 1.0 ml of a pesticide solution. Two mixtures of pesticides were used. One of the solutions contained CIPC, atrazine and simazine dissolved in methyl alcohol, and the other contained trifluralin, IPC and PCNB dissolved in 4% ethyl alcohol in hexane. The water samples were fortified at 100 ppt, 400 ppt, 1.0 ppb and 10.0 ppb. Two grams of NaCl were added to each sample. The samples were extracted 3x with 50 ml of methylene chloride. The extracts were combined, dried with $Na_2SO_4$ and evaporated to near dryness on a rotary evaporator. The reduced extract was then quantitatively transferred to a 15-ml culture tube that contained 1 ml of a 1% solution of pentadecane in hexane. The extract was evaporated with a gentle stream of dry air (filtered with Florisil) and the residue dissolved in hexane (1.0 or 10.0 ml).

Recoveries of nitrogen-containing pesticides from water are shown in Table XXXVIII. In general, recoveries increased with concentration for all compounds. The relatively low recoveries obtained at the 100 ppt level were due to pesticide loss during evaporation of the solvent. When compared to controls that were treated in the same manner as the water samples (except no water was envolved), recoveries were essentially 100% for all compounds. The effect of greater concentrations of pentadecane or more

Table XXXVIII. Recovery of Nitrogen-Containing Pesticides from Water.

| Pesticide | % Recovery[a] | | | |
|---|---|---|---|---|
| | 100 ppt | 400 ppt | 1 ppb | 10 ppb |
| CIPC | 70 | -- | 83 | 87 |
| Atrazine | 68 | 91 | 85 | 97 |
| Simazine | 64 | 85 | 85 | 90 |
| Trifluralin | 49 | 60 | 66 | 77 |
| IPC | 46 | 51 | 58 | 72 |
| PCNB | 45 | 55 | 67 | 68 |

[a] Recoveries are the average of three replicates.

efficient "keepers" was not studied, but probably would result in improved recoveries. Representative chromatograms of the water extracts are reproduced in Figures 64 and 65.

Analysis of Nitrogen-Containing Pesticides in Soil. Soil samples (25 g) were fortified at 0.02 (0.01 for atrazine and simazine), 0.1, 1.0 and 10.0 ppm by the addition of 1.0 ml of methanolic solutions of the same two pesticide mixtures as used in the water analysis. The samples were extracted as described for the analysis of halogen- and sulfur-containing pesticides in soil. The concentrated extract was cleaned up on a as-received Florisil column. The Florisil column contained approximately 1 in. of $Na_2SO_4$ on the top and 5 g of Florisil. The extract was transferred to the column with approximately 2 ml of benzene, and the pesticides eluted with an additional 20 ml of benzene. The benzene was evaporated and the residue dissolved in hexane (1.0 or 10.0 ml) for gas chromatographic analysis.

Recoveries of nitrogen-containing pesticides from soil are summarized in Table XXXIX. Recoveries ranged from 51% for IPC at 0.02 ppm to 93% for trifluralin at 1.0 ppm. Recoveries for IPC and PCNB were relatively low for 0.02 and 0.1 ppm. The low recovery was due in part to pesticide loss on the cleanup column. Approximately 25 to 30% of IPC and 10 to 20% of PCNB were lost on the cleanup column (compare the 1.0 and 10.0 ppm levels with the 0.02 and 0.1 ppm levels). The other nitrogen-containing pesticides were recovered from the cleanup column with little loss. Representative chromatograms of the soil extracts are shown in Figures 66 and 67.

Analysis of Nitrogen-Containing Pesticides in Alfalfa. Alfalfa samples (10 g) were fortified with two pesticide mixtures. CIPC, atrazine and simazine constituted one mixture, and trifluralin, IPC and PCNB constituted

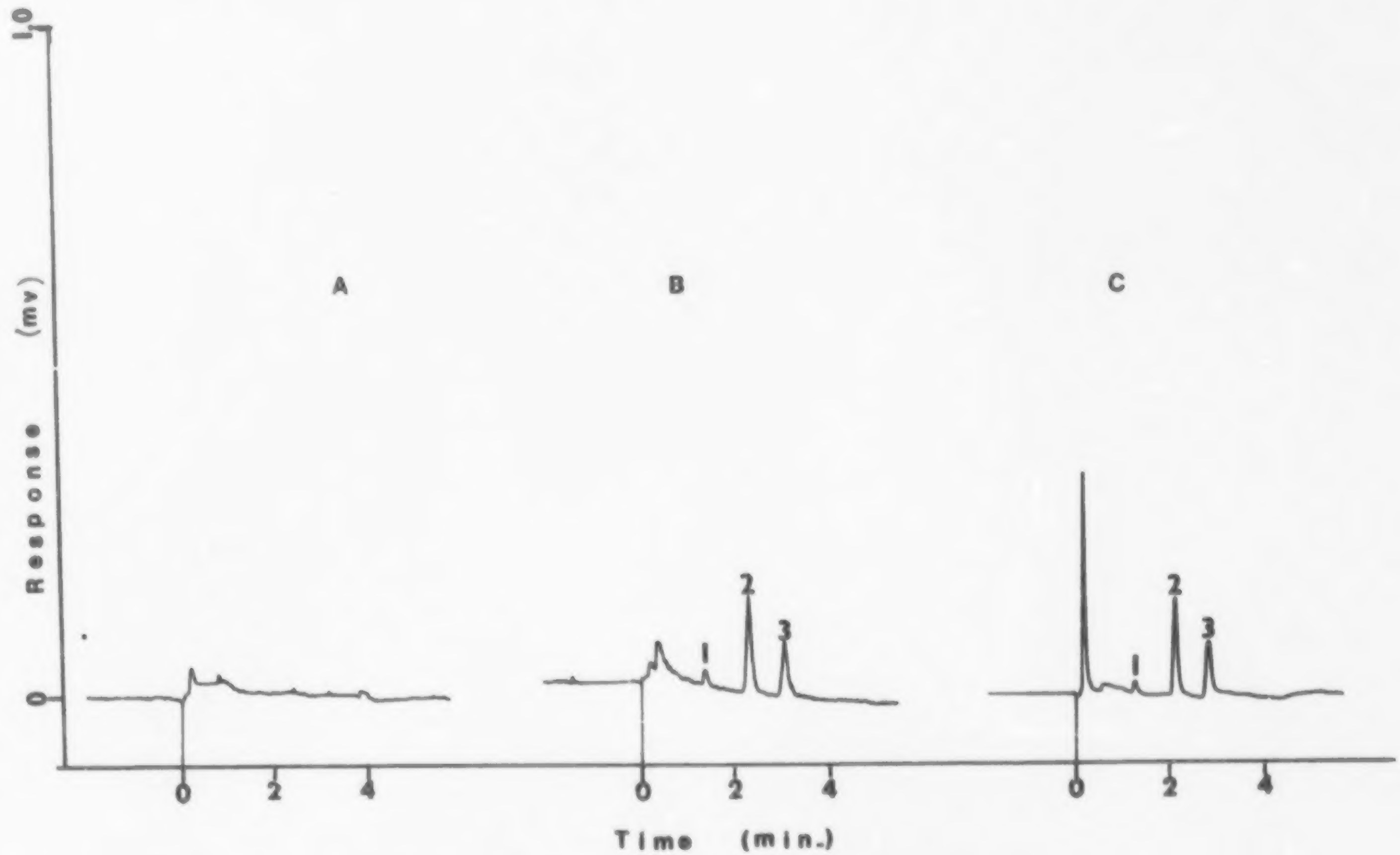


Figure 64. Chromatograms of CIPC (1), atrazine (2) and simazine (3) extracted from water. Sample: A, control, attenuation = 10 X 0.2; B, 100 ppt, attenuation = 10 X 0.2; C, 1 ppb, attenuation = 10 X 0.4.

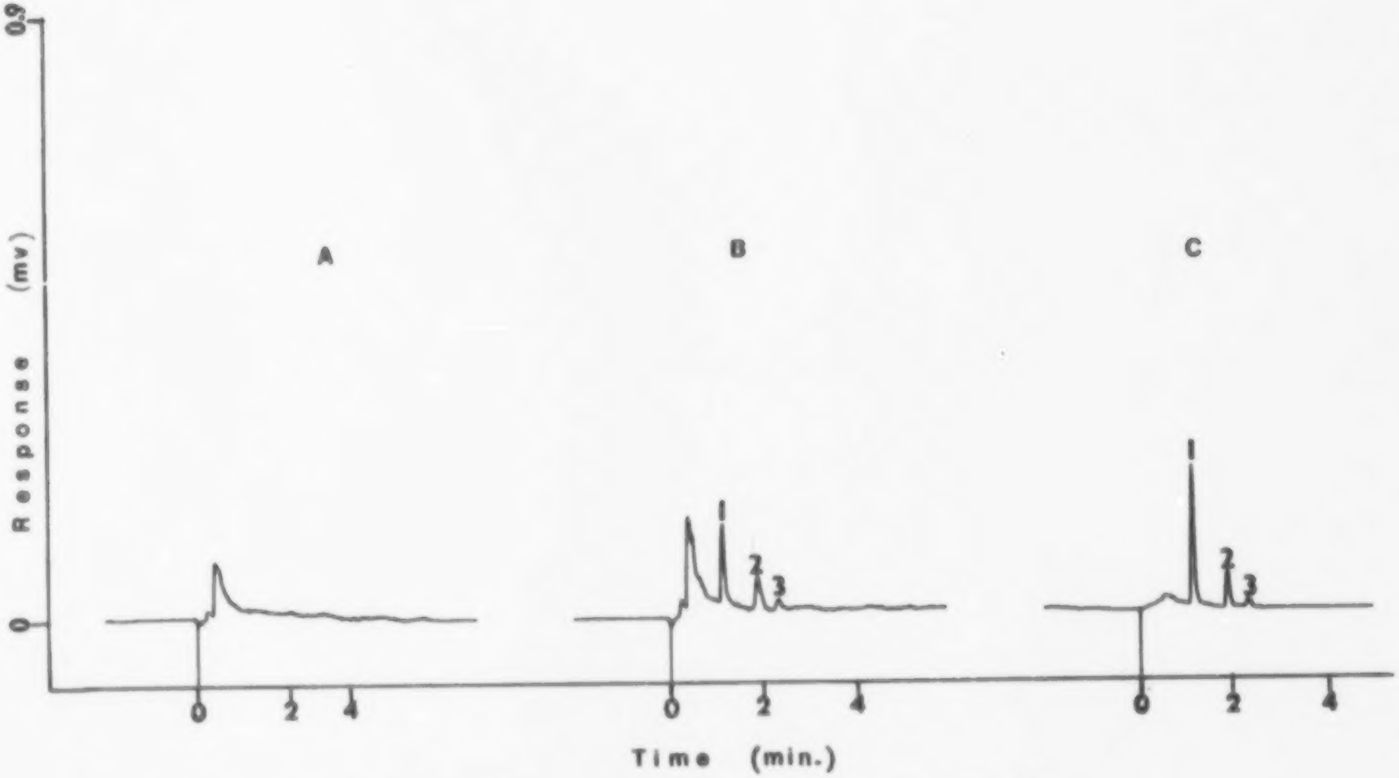


Figure 65. Chromatograms of trifluralin (1), IPC (2) and PCNB (3) extracted from water. Sample: A, control, attenuation = 10 X 0.2; B, 100 ppt, attenuation = 10 X 0.2; C, 1 ppb, attenuation = 10 X 0.2.

Table XXXIX. Recovery of Nitrogen-Containing Pesticides from Soil.

| Pesticide | % Recovery[a] | | | |
|---|---|---|---|---|
| | 0.02 ppm | 0.1 ppm | 1.0 ppm | 10.0 ppm |
| CIPC | -- | 75 | 63 | 69[c] |
| Atrazine | 83[b] | 77 | 75 | 75[c] |
| Simazine | 76[b] | 69 | 70 | 79[c] |
| Trifluralin | 68 | 81 | 93[c] | 85[c] |
| IPC | 51 | 51 | 81[c] | 75[c] |
| PCNB | 60 | 65 | 80[c] | 70[c] |

[a] Recoveries are the average of three replicates.

[b] Recovery is for 0.01 ppm.

[c] No cleanup procedure was used.

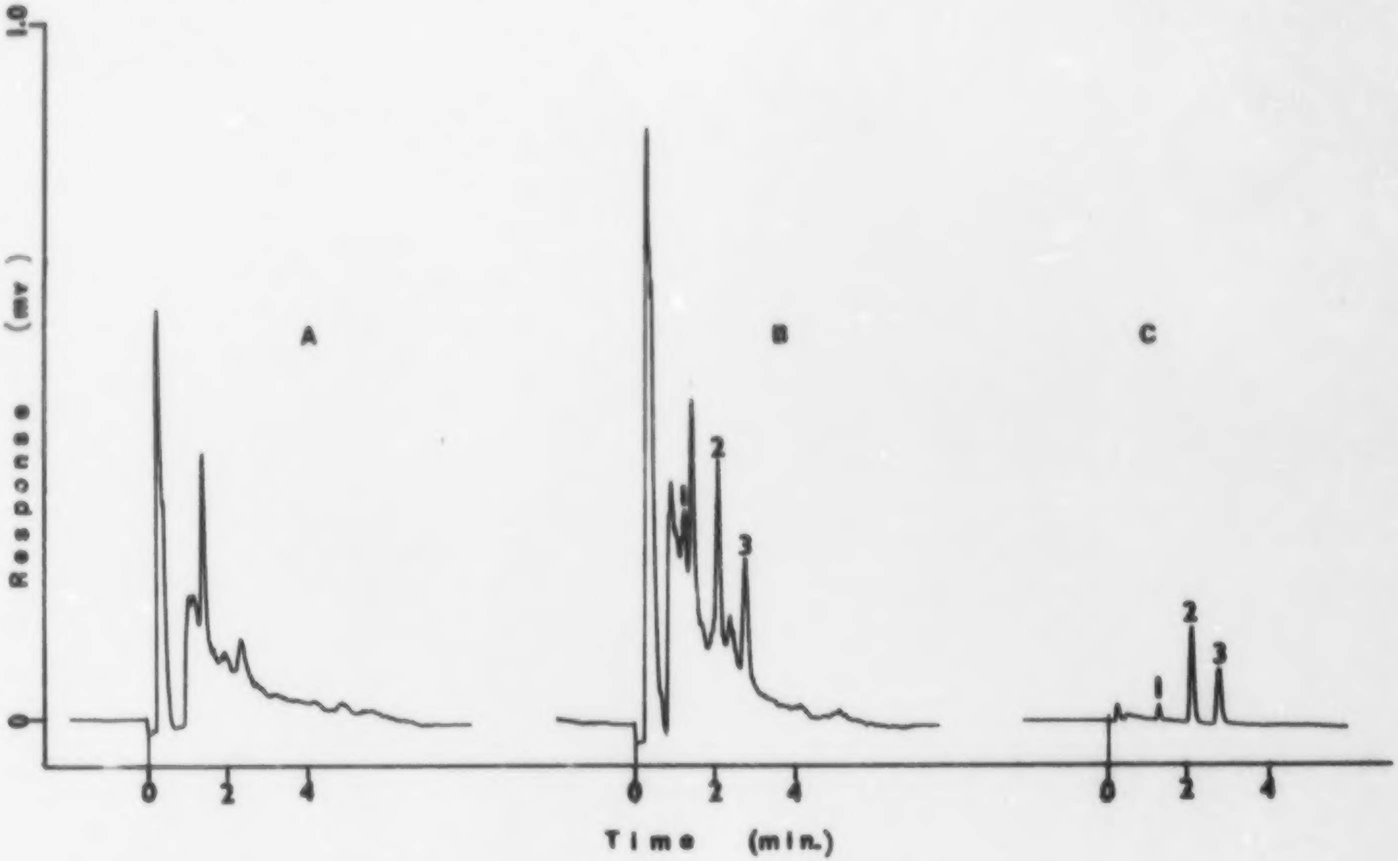


Figure 66. Chromatograms of CIPC (1), atrazine (2) and simazine (3) extracted from soil. Sample: A, control, attenuation = 10 X 0.2; B, 0.01 ppm, attenuation = 10 X 0.2; C, 1 ppm, attenuation = 10 X 0.8.

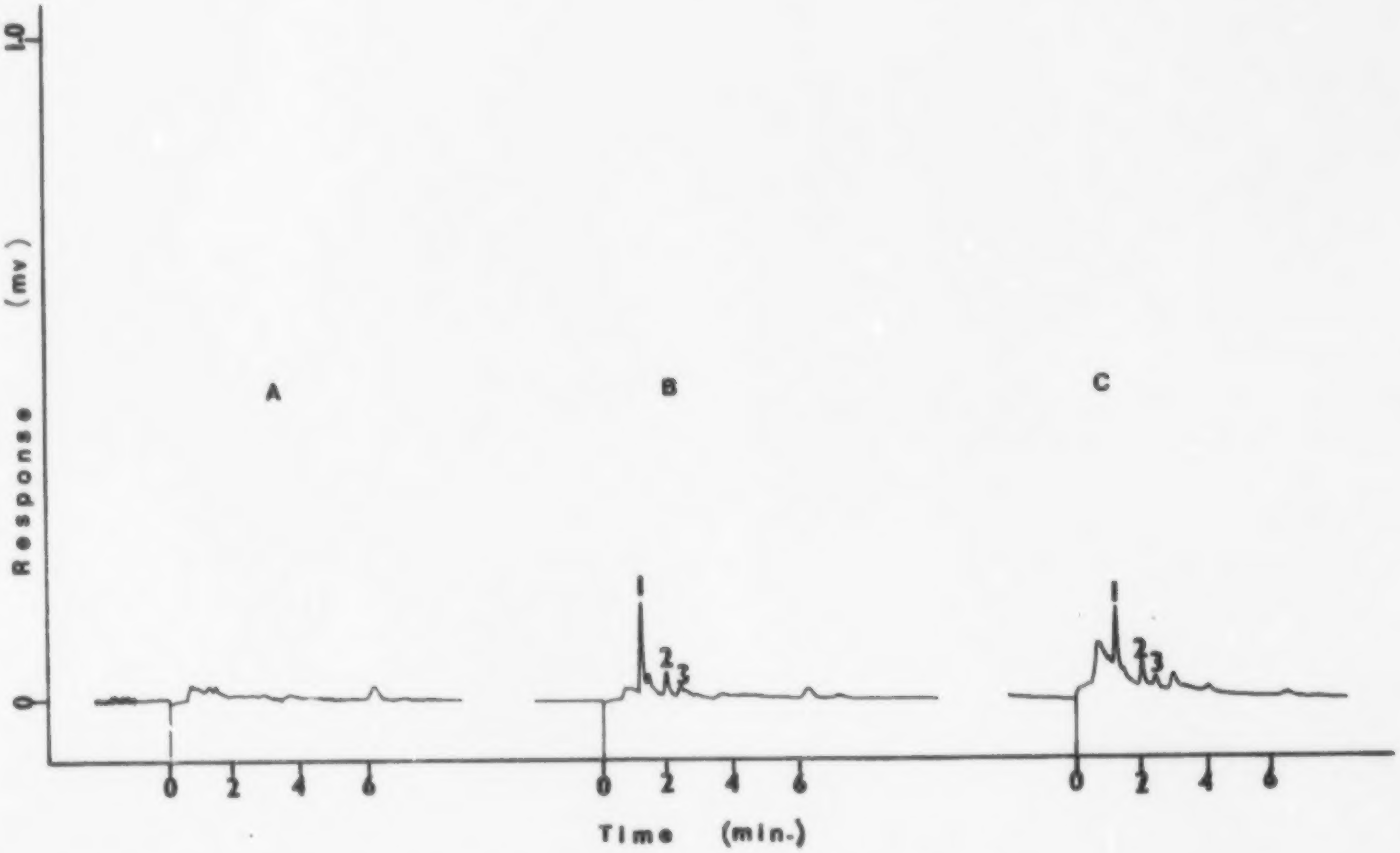


Figure 67. Chromatograms of trifluralin (1), IPC (2) and PCNB (3) extracted from soil. Sample: A, control, attenuation = 10 X 0.4; B, 0.02 ppm, attenuation = 10 X 0.4; C, 1 ppm, attenuation = 10 X 0.8.

the other. The samples were extracted and cleaned up as described for the analysis of sulfur-containing pesticides in alfalfa.

The recoveries that were obtained are presented in Table XL. Recoveries ranged from 65% for CIPC and simazine at 0.01 ppm to 101% for PCNB at 0.02 ppm. There did not appear to be any distinct correlation between the quantity of pesticide recovered and the level at which the samples were fortified.

As shown in Figures 68 and 69, there are several peaks from the alfalfa that can interfere with the analysis of nitrogen compounds at the 0.01 to 0.02 ppm level. The interference peak between trifluralin and IPC exhibited considerable variability, whereas the interference peak after PCNB was fairly consistent. The interference peaks at the same retention times of atrazine and simazine were also fairly constant, and were equivalent to approximately 0.002 ppm of these pesticides.

Table XL. Recovery of Nitrogen-Containing Pesticides from Alfalfa.

| Compound | % Recovery[a] | | | | |
|---|---|---|---|---|---|
| | 0.01 ppm | 0.02 ppm | 0.1 ppm | 1.0 ppm | 10.0 ppm |
| CIPC | 65 | -- | 73 | 76 | 77 |
| Atrazine | 81 | -- | 78 | 82 | 94 |
| Simazine | 65 | -- | 72 | 80 | 90 |
| Trifluralin | -- | 82 | 79 | 74 | 88 |
| IPC | -- | 92 | -- | 70 | 81 |
| PCNB | — | 101 | 97 | 74 | 83 |

[a] Recoveries are the average of three replicates.

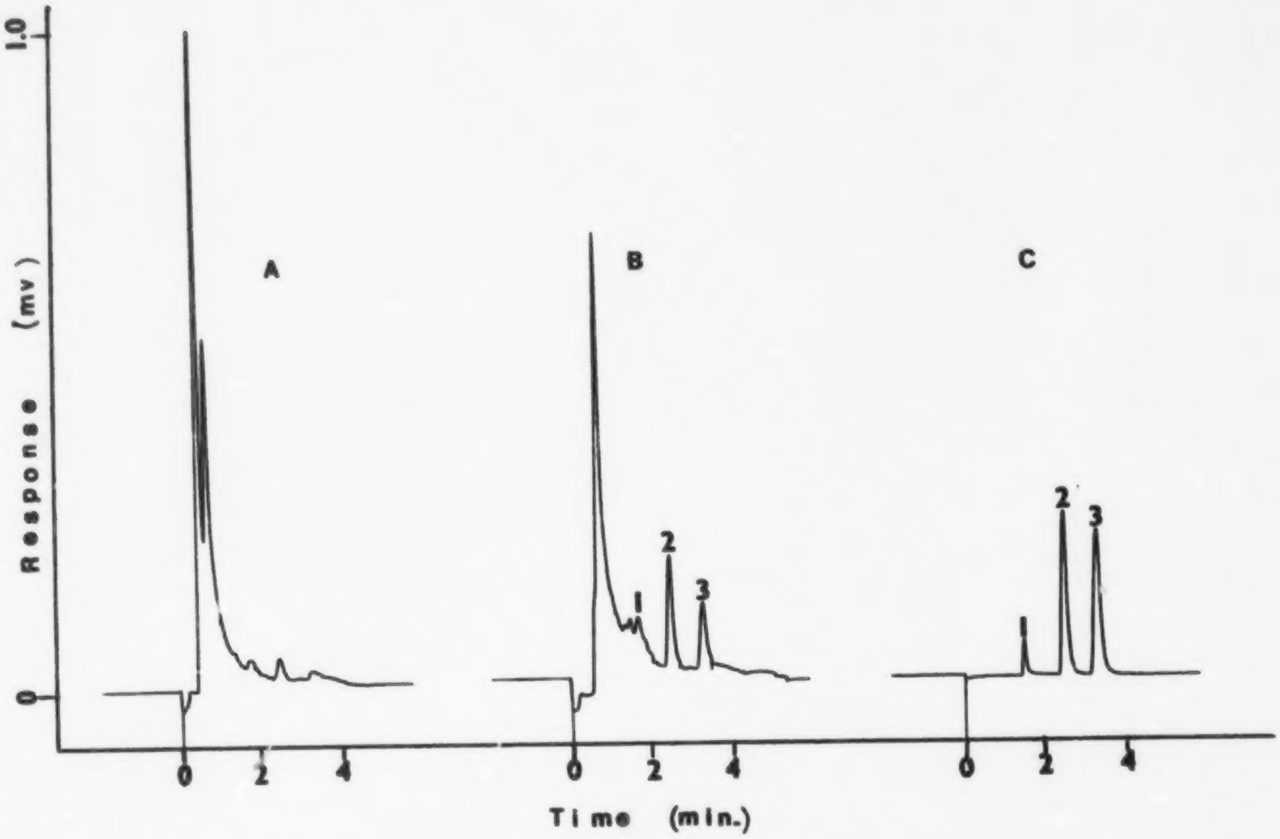


Figure 68. Chromatograms of CIPC (1), atrazine (2) and simazine (3) extracted from alfalfa. Sample: A, control, attenuation = 3 X 0.2; B, 0.01 ppm, attenuation = 3 X 0.2; C, 1 ppm, attenuation = 100 X 0.2.

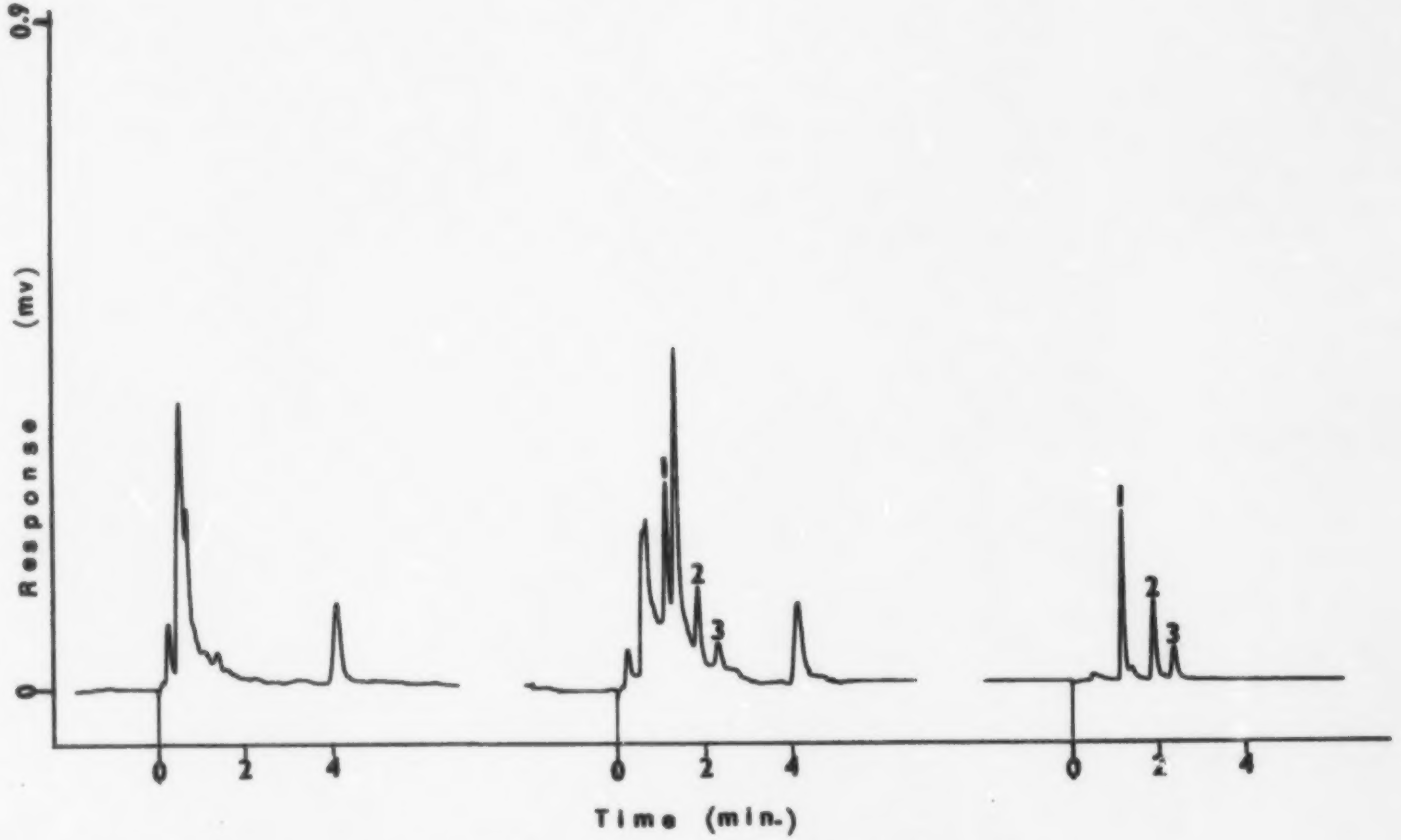


Figure 69. Chromatograms of trifluralin (1), IPC (2) and PCNB (3) extracted from alfalfa. Sample: A, control, attenuation = 10 X 0.1; B, 0.02 ppm, attenuation = 10 X 0.1; C, 1 ppm, attenuation = 10 X 1.6.

## RECOMMENDED OPERATING CONDITIONS AND MAINTENANCE

The electrolytic conductivity detector can be used for the selective detection of halogen-, sulfur-, nitrogen- and ester-containing compounds. It can also be used for the general detection of organic compounds and the selective detection of certain compounds in the presence of other compounds that contain the same element (such as nitrosamines in the presence of other nitrogen compounds[6] and aliphatic chlorine compounds in the presence of aromatic chlorine compounds[7]). Response to a given element depends upon the specific operating conditions employed. However, the same conditions are not necessarily optimum for both sensitivity and specificity. Thus, the utilization of generalized operating parameters for a given element may not be sufficient for certain analyses.

Although a given set of operating parameters may not be sufficient for all analyses, certain operating procedures provide superior detector performance. For instance, nickel tubing and soxhlet extracted ion exchange resins are recommended for the detection of halogen and sulfur compounds. Stacked ion exchange resin beds are recommended for the maintenance of a pH below 7.0 for halogen and sulfur compounds and above a pH of 7.0 for nitrogen compounds. Specific operating conditions for the detection of halogen-, sulfur-, and nitrogen-containing compounds are listed below.

Detection of Halogen Compounds. Slightly different operating parameters are recommended for a) the general detection of halogen-containing compounds with maximum specificity, b) the general detection of halogen-containing compounds with maximum sensitivity and peak sharpness,

c) selective detection of aliphatic chlorine compounds in the presence of aromatic chlorine compounds with maximum selectivity to chlorine, and

d) selective detection of aliphatic chlorine compounds in the presence of aromatic chlorine compounds with maximum sensitivity and peak sharpness.

General Detection of Halogen Compounds with Maximum Specificity:

Reaction Tube[a]: Nickel (1/16 in. o.d. x 0.02 in. i.d.)

Reaction Gas: Electrolytic hydrogen

Reaction Gas Flow Rate: 100 cc/min.

Carrier Gas: High purity helium

Furnace Temperature: 840 - 860°

Conductivity Solvent: n-Butyl alcohol

Conductivity Solvent Flow Rate: 0.6 cc/min.

Ion Exchange Resin[b]: 65% IRN-77 on pump side and 35% IRN-150 on cell side of resin tube

Injection Solvent Vent: Yes

Interfering Elements: Negative peaks from large quantities of nitrogen compounds.

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[a] Nickel reaction tube will take at least two days to condition and may take as long as 10 days.

[b] Resins soxhlet extracted with water and methyl alcohol.

General Detection of Halogen Compounds with Maximum Sensitivity:

Reaction Tube: Nickel (1/16 in o.d. x 0.02 in. i.d.)

Reaction Gas: Electrolytic hydrogen

Reaction Gas Flow Rate: 100 cc/min.

Carrier Gas: Electrolytic hydrogen or high purity helium

Furnace Temperature: 840 - 860°

Conductivity Solvent: Methyl alcohol

Conductivity Solvent Flow Rate: 0.4-0.6 cc/min.

Ion Exchange Resin: 65% soxhlet extracted IRN-77 on pump side and 35% soxhlet extracted IRN-150 on cell side

Injection Solvent Vent: Yes

Interfering Elements: Large quantities of nitrogen-, sulfur- and ester-containing compounds may give interference

Selective Detection of Aliphatic Chlorine with Maximum Specificity to Chlorine:

Reaction Tube: Nickel (1/16 in. o.d. x 0.02 in. i.d.)

Reaction Gas: Air

Reaction Gas Flow Rate: 100 cc/min

Carrier Gas: High purity helium

Furnace Temperature[a]: 750 - 800°

Conductivity Solvent: n-Butyl alcohol

Conductivity Solvent Flow Rate: 0.6 cc/min.

Ion Exchange Resin: 65% soxhlet extracted IRN-77 on pump side and 35% soxhlet extracted IRN-150 on cell side

Injection Solvent Vent: Yes

Interfering Elements: Sulfur compounds and large quantities of certain nitrogen containing compounds.

Selective Detection of Aliphatic Chlorine with Maximum Sensitivity.

Reaction Tube: Nickel (1/16 in. o.d. x 0.02 in. i.d.)

Reaction Gas: Air

Reaction Gas Flow Rate: 100 cc/min.

Carrier Gas: High purity helium

Furnace Temperature: 780 - 800°

Conductivity Solvent: Methyl alcohol

Conductivity Solvent Flow Rate: 0.4-0.6 cc/min.

Ion Exchange Resin: 65% soxhlet extracted IRN-77 on pump side and 35% soxhlet extracted IRN-150 on cell side

Injection Solvent Vent: Yes

Interferring Elements: Sulfur compound and large quantities of certain nitrogen- and ester-containing compounds

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[a] The lower temperature results in greater selectivity, but may greatly reduce response to certain aliphatic chlorine compounds.

*Detection of Sulfur-Containing Compounds*. The following operating parameters are recommended for the detection of sulfur-containing compounds.

Reaction Tube: Nickel (1/16 in. o.d. x 0.02 in. i.d.)

Reaction Gas: Air

Reaction Gas Flow Rate: 100 cc/min.

Carrier Gas: High purity Helium

Furnace Temperature: 650 - 800$^0$

Conductivity Solvent: Methyl alcohol

Conductivity Solvent Flow Rate: 0.4-0.6 cc/min.

Ion Exchange Resin: 65% soxhlet extracted IRN-77 on pump side and 35% soxhlet extracted IRN-150 on cell side

Injection Solvent Vent: Yes

Interferring Elements: Chlorine and large quantities of certain nitrogen- and ester-containing compounds

Two furnace temperatures are recommended. A furnace temperature of 650$^0$ gives the best selectivity and only certain types of halogen, nitrogen and ester compounds will interfere. However, sensitivity at 650$^0$ is only 25 to 40% of that at higher temperatures. Consequently, a furnace temperature of 800$^0$ is recommended for greater sensitivity but less specificity.

*Detection of Nitrogen Compounds*. Although only one set of conditions is recommended for the detection of nitrogen compounds, certain modifications of operating parameters may be required. For instance, if there is contaminant bleed into the furnace that results in acidic reaction products, a small amount of nitrogen (0.01 to 0.1 cc/min.) may have to be added to the reaction gas to compensate for the elevated acidity. The recommended operating conditions are:

Reaction Tube: Quartz (1/8 in. o.d. x 2 mm. i.d.)
Catalyst: Nickel wire strands (0.12 mm. or 0.25 mm. o.d. x ~ 1 in.)
Reacting Gas: Electrolytic hydrogen
Reaction Gas Flow Rate: 60 - 80 cc/min.
Carrier Gas: Electrolytic hydrogen or ultra-high purity helium.
Furnace Temperature: $820 - 850^0$
Conductivity Solvent: 15% Isopropyl alcohol
Conductivity Solvent Flow Rate: 0.4-0.6 cc/min.
Ion Exchange Resin: 70% IRN-78 or ARA-366 and 30% IRN-150
Scrubber: 10% Sr(OH) on glass wool
Scrubber Position: Just within furnace end plate
Injection Solvent Vent: yes
Interferring Elements: Large quantities of sulfur compounds

Detector Maintenance. In general, the only maintenance required for the detection of halogen and sulfur compounds is a) replenishment of the conductivity solvent, b) replacement of the conductivity solvent approximately once a month, and c) replacement of the ion exchange resin approximately every three to six weeks. The Teflon transfer lines and conductivity cell usually do not become contaminated, but should be cleaned with $H_3PO_4$ if contamination is suspected.

The detection of nitrogen compounds requires a) replenishment of the conductivity solvent, b) replacement of the conductivity solvent approximately every two weeks, c) replacement of the scrubber as required, usually every two to four weeks for residue analyses, and d) replacement of the ion exchange resin approximately every three months. The catalyst usually lasts for six months to a year, but can be poisoned by column bleed and other contaminants. Thus, the catalyst may require more frequent replacement.

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